Supporting information for the paper

Fast Computation of Solvation Free Energies with Molecular Density Functional Theory: Thermodynamic-Ensemble Partial Molar Volume Corrections

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1 Grand Potential with respect to uniform density

The free energy functional is defined as follows:

$$\mathcal{F}[\boldsymbol{\rho}] = kT \int (\rho(1) \ln \Lambda^3 \Lambda_{rot} \rho(1) - \rho(1)) d1 + \int \rho(1) v(1) d1 + \mathcal{F}^{exc}[\boldsymbol{\rho}] \tag{1}$$

In the HNC approximation , $\mathcal{F}^{exc}$ is represented by its first two terms in the Taylor series around the uniform density ρ_0:

$$\mathcal{F}^{exc}[\boldsymbol{\rho}] = \mathcal{F}^{exc}[\rho_0] + \int \left. \frac{\delta \mathcal{F}^{exc}}{\delta \rho(1)} \right|_{\rho_0} \Delta\rho(1) d1 + \frac{1}{2} \int \Delta\rho(1) \frac{\delta^2 \mathcal{F}^{exc}}{\delta\rho(1)\delta\rho(2)} \Delta\rho(2) d1 d2 \tag{2}$$

where

$$\frac{\delta \mathcal{F}^{exc}}{\delta \rho(1)} \equiv -kT c^{(1)}(1) = \text{const} \tag{3}$$

$$\frac{\delta^2 \mathcal{F}^{exc}}{\delta\rho(1)\delta\rho(2)} \equiv -kT c(12) \tag{4}$$

We are interested not in the absolute free energy $\mathcal{F}[\boldsymbol{\rho}]$, but in the free-energy change $\Delta\mathcal{F}[\boldsymbol{\rho}]$ with respect to uniform density:

$$\Delta\mathcal{F}[\boldsymbol{\rho}] = \mathcal{F}[\boldsymbol{\rho}] - \mathcal{F}[\rho_0] \tag{5}$$

Using the definition of free energy functional we find

$$\begin{aligned} \Delta\mathcal{F}[\boldsymbol{\rho}] &= kT \int (\rho(1) \ln \Lambda^3 \Lambda_{rot} \rho(1) - \rho(1)) d1 - kT \int (\rho_0 \ln \Lambda^3 \Lambda_{rot} \rho_0 - \rho_0) d1 \\ &+ \int \rho(1) v(1) d1 + \mathcal{F}^{exc}[\boldsymbol{\rho}] - \mathcal{F}^{exc}[\rho_0] \end{aligned} \tag{6}$$

Subtracting and adding $kT \int \rho(1) \ln \Lambda^3 \Lambda_{rot} \rho_0 d1$ to the ideal part we get

$$\begin{aligned} kT \int (\rho(1) \ln \Lambda^3 \Lambda_{rot} \rho(1) - \rho(1)) d1 &- kT \int (\rho_0 \ln \Lambda^3 \Lambda_{rot} \rho_0 - \rho_0) d1 = \\ kT \int (\rho(1) \ln \Lambda^3 \Lambda_{rot} \rho(1) - \rho(1) \ln \Lambda^3 \Lambda_{rot} \rho_0) d1 &+ kT \int (\rho(1) \ln \Lambda^3 \Lambda_{rot} \rho_0 - \rho_0 \ln \Lambda^3 \Lambda_{rot} \rho_0) d1 - \int \Delta\rho(1) d1 = \\ kT \int (\rho(1) \ln \frac{\rho(1)}{\rho_0} - \Delta\rho(1)) d1 &+ kT \ln \Lambda^3 \Lambda_{rot} \rho_0 \int \Delta\rho(1) d1 \end{aligned} \tag{7}$$

Using the definition of excess free energy (2), we write the excess part as follows:

$$\mathcal{F}^{exc}[\boldsymbol{\rho}] - \mathcal{F}^{exc}[\rho_0] = \left. \frac{\delta \mathcal{F}^{exc}}{\delta \rho} \right|_{\rho_0} \int \Delta\rho(1) d1 - \frac{kT}{2} \int \Delta\rho(1) c(12) \Delta\rho(2) d1 d2 \tag{8}$$

Substituting expressions (7),(8) into (6) we obtain the following formula for the free energy change:

$$\Delta\mathcal{F}[\boldsymbol{\rho}] = kT \int (\rho(1) \ln \frac{\rho(1)}{\rho_0} - \Delta\rho(1)) d1 + \int \rho(1) v(1) d1 - \frac{kT}{2} \int \Delta\rho(1) c(12) \Delta\rho(2) d1 d2 + \lambda \int \Delta\rho(1) d1 \tag{9}$$

where

$$\lambda \equiv kT \ln \Lambda^3 \Lambda_{rot} \rho_0 + \left. \frac{\delta \mathcal{F}^{exc}}{\delta \rho} \right|_{\rho_0} \tag{10}$$

The grand potential $\Theta[\boldsymbol{\rho}]$ is defined as

$$\Theta[\boldsymbol{\rho}] = \mathcal{F}[\boldsymbol{\rho}] - \mu_0 \int \rho(1) d1 \tag{11}$$

Using the fact that for the uniform fluid the minimum of the potential is at $\boldsymbol{\rho} = \rho_0$, we have

$$\left. \frac{\delta \Theta}{\delta \rho(1)} \right|_{\rho_0} = kT \ln \Lambda^3 \Lambda_{rot} \rho_0 + \left. \frac{\delta \mathcal{F}^{exc}}{\delta \rho} \right|_{\rho_0} - \mu_0 = 0 \tag{12}$$

This gives $\mu_0 = \lambda$. Then the grand potential change $\Delta\Theta[\boldsymbol{\rho}] \equiv \Theta[\boldsymbol{\rho}] - \Theta[\rho_0]$ is written as follows:

$$\begin{aligned} \Delta\Theta[\boldsymbol{\rho}] &= \Delta\mathcal{F} - \mu_0 \int \Delta\rho(1) d1 = \\ kT \int (\rho(1) \ln \frac{\rho(1)}{\rho_0} - \Delta\rho(1)) d1 &+ \int \rho(1) v(1) d1 - \frac{kT}{2} \int \Delta\rho(1) c(12) \Delta\rho(2) d1 d2 \end{aligned} \tag{13}$$

2 Gibbs Free Energy of the uniform fluid

Free energy of the uniform fluid includes ideal and excess components. Ideal part is known: for the fluid of density n_0 in the volume V it is written as follows:

$$F_V^{id}[n_0] = NkT \ln \Lambda^3 \Lambda_{rot} \rho_0 - NkT = n_0 kTV \ln \Lambda^3 \Lambda_{rot} \rho_0 - n_0 VkT \tag{14}$$

where $\rho_0 = n_0/\Phi$, $\Phi = \int d\Omega$, $N = n_0 V$.
To find the excess part, we can write expression (2) for the density $\boldsymbol{\rho} = 0$, $\Delta\rho(1) = (-\rho_0)$:

$$F_V^{exc}[0] = F_V^{exc}[\rho_0] + \left. \frac{\delta \mathcal{F}^{exc}}{\delta \rho} \right|_{\rho_0} \int_{V \times \Phi} (-\rho_0) d1 - \frac{kT}{2} \int_{(V \times \Phi)^2} \rho_0^2 c(12) d1 d2 \tag{15}$$

Using the uniformity of $c(12)$ we have:

$$\int_{V \times \Phi} \int_{V \times \Phi} c(12) d1 d2 = V \int_{V \times \Phi^2} c(\mathbf{r_{12}}, \Omega_1, \Omega_2) d\mathbf{r_{12}} d\Omega_1 d\Omega_2 = V \Phi^2 \hat{c}_S(k=0) \tag{16}$$

where $c_S(r_{12}) = \Phi^{-2} \int d\Omega_1 d\Omega_2 c(12)$.
Inserting this into (15) we find the following relation for $F^{exc}[\rho_0]$:

$$F_V^{exc}[\rho_0] = \left. \frac{\delta \mathcal{F}^{exc}}{\delta \rho} \right|_{\rho_0} n_0 V + \frac{kT}{2} n_0^2 V \hat{c}_S(k=0) \tag{17}$$

Combining the ideal and excess parts, we get the following expression for the free energy of a uniform fluid at density ρ_0:

$$F_V[\rho_0] = \mu_0 N - n_0 VkT + \frac{kT}{2} n_0^2 V \hat{c}_S(k=0) \tag{18}$$

where $N = n_0 V$, and μ_0 is defined as previously. This gives the following expression for the Gibbs free energy of the uniform fluid of volume V and density ρ_0:

$$G_V[\rho_0] = F_V[\rho_0] + PV = \mu_0 N \tag{19}$$

where we use the following pressure representation:

$$P \equiv P^{id} + P^{exc} = n_0 kT + P^{exc}[n_0] \tag{20}$$

and $P^{exc} = -\frac{kT}{2} n_0^2 \hat{c}(k=0)V$ (see next section for derivation).

3 Pressure in the Homogeneous Reference Fluid Approximation

To calculate pressure, we need to take a derivative of the free energy with respect to volume at constant number of particles. The density in this process will change, so we need another expression for the free energy. Let the density n_0 corresponds to N_0 particles in a volume V_0:

$$n_0 = \frac{N_0}{V_0} \tag{21}$$

Let us now find the functional for the uniform fluid in a larger box of volume V at density $n_1 = N/V$. The ideal-part free energy is known, and in this case, reads

$$F^{id}(N,V) = NkT \ln \Lambda^3 \Lambda_{rot} \frac{N}{V\Phi} - NkT \tag{22}$$

where $\rho_1 = n_1/\Phi$, $\Phi = \int d\Omega$. To find the excess part, we can use relation (2):

$$F^{exc}(N,V) = F^{exc}(\rho_0, V) + \left.\frac{\delta \mathcal{F}^{exc}}{\delta \rho}\right|_{\rho_0} \int_{V\times\Phi} (\rho_1 - \rho_0) d1 - \frac{kT}{2}(\rho_1 - \rho_0)^2 \int_{(V\times\Phi)^2} c(12) d1 d2 \tag{23}$$

where

$$\rho_1 - \rho_0 = \frac{1}{\Phi}\left(\frac{N}{V} - \frac{N_0}{V_0}\right) = \frac{1}{\Phi}\frac{NV_0 - N_0 V}{V_0 V} \tag{24}$$

This gives the following expression for the free energy:

$$F^{exc}(N,V) = \left.\frac{\delta \mathcal{F}^{exc}}{\delta \rho}\right|_{\rho_0} n_0 V + \frac{kT}{2} n_0^2 V \hat{c}_S(k=0) + \left.\frac{\delta \mathcal{F}^{exc}}{\delta \rho}\right|_{\rho_0} \frac{NV_0 - N_0 V}{V_0} - \frac{kT}{2}\frac{(NV_0 - N_0 V)^2}{V_0^2 V}\hat{c}_S(k=0) \tag{25}$$

where $c_S(r_{12}) = \int c(r_{12}, \Omega_1, \Omega_2) d\Omega_1 d\Omega_2$.

Pressure is minus derivative of the Helmholtz Free Energy over the volume at constant number of particles. The result for the ideal part is known:

$$P^{id}(N,V) = -\frac{\partial F^{id}(N,V)}{\partial V} = \frac{N}{V} kT \tag{26}$$

For the excess part we have:

$$P^{exc} = -\frac{\partial F^{exc}}{\partial V} = \left.\frac{\delta \mathcal{F}^{exc}}{\delta \rho}\right|_{\rho_0} \frac{N_0}{V_0} + \frac{kT}{2}\hat{c}_S(k=0)\left(\frac{2(NV_0 - N_0 V)(-N_0)}{V_0^2 V} - \frac{(NV_0 - N_0 V)^2}{V_0^2 V^2}\right) \tag{27}$$

$$- \left.\frac{\delta \mathcal{F}^{exc}}{\delta \rho}\right|_{\rho_0} \rho_0 - \frac{kT}{2}\hat{c}_S(k=0)\rho_0^2 \tag{28}$$

The second term is:

$$\frac{kT}{2}c(k=0)\frac{NV_0 - N_0V}{V_0V}\left(\frac{-2N_0}{V_0} - \frac{NV_0 - N_0V}{V_0V}\right) \tag{29}$$

$$= \frac{kT}{2}c(k=0)(\rho-\rho_0)(-2\rho_0 - \rho + \rho_0) = \frac{kT}{2}c(k=0)(\rho_0^2 - \rho^2) \tag{30}$$

Finally, we get the following expression for the excess pressure:

$$P^{exc} = \frac{kT}{2}c(k=0)(\rho_0^2 - \rho^2) - \frac{kT}{2}c(k=0)\rho_0^2 = -\frac{kT}{2}c(k=0)\rho^2 \tag{31}$$

The total pressure is a sum of the ideal and excess parts:

$$P(N,V) = P^{id} + P^{exc} = \frac{N}{V}kT - \frac{kT}{2}c(k=0)\left(\frac{N}{V}\right)^2 \tag{32}$$

4 Pressure of the inhomogeneous fluid

The previous derivation is valid for the homogeneous fluid with density N/V. For inhomogeneous fluid we cannot define the liquid pressure: it is different at different parts of the system. To find the pressure contribution to the free energy in this case we use the expression for the free energy [1]:

$$F_V[\rho] = F^{id} + F_V^{exc}[\rho_0] + \left.\frac{\delta \mathcal{F}^{exc}}{\delta \rho}\right|_{\rho_0}\int_V \Delta\rho - \frac{kT}{2}\int_V\int_V \Delta\rho(1)c(12)\Delta\rho(2)d12 \tag{33}$$

where

$$F^{id} = kT\int \rho \ln \Lambda^3\rho - kT\int\rho + \int \rho U \tag{34}$$

$$F_V^{exc}[\rho_0] = \left.\frac{\delta \mathcal{F}^{exc}}{\delta \rho}\right|_{\rho_0} n_0V + \frac{kT}{2}n_0^2\hat{c}_S(k=0)V \tag{35}$$

and $c_S(r_{12}) = \Phi^{-2}\int d\Omega_1 d\Omega_2 c(12)$.

We divide the volume into elementary volumes V_i, at each element density is constant ρ_i, and $n_i = \rho_i V_i$ is the number of particles in that volume. In that case free energy can be rewritten in a following way :

$$\begin{gathered} F[n_1,\ldots,n_M,V_1,\ldots,V_M] = \\ kT\sum_i \rho_i V_i \ln\Lambda^3\frac{n_i}{v_i} - kT\sum_i \rho_i V_i + \sum \rho_i V_i U(i) \\ + \left.\frac{\delta \mathcal{F}^{exc}}{\delta \rho}\right|_{\rho_0}\rho_0\sum_i V_i + \frac{kT}{2}\rho_0^2 c(k=0)\sum_i V_i \\ + \left.\frac{\delta \mathcal{F}^{exc}}{\delta \rho}\right|_{\rho_0}\sum_i(\rho_i-\rho_0)V_i - \frac{kT}{2}\sum_i(\rho_i-\rho_0)V_i\int_V \Delta c(i2)\Delta\rho(2)d2 \end{gathered} \tag{36}$$

Taking derivative over V_i (and considering $\rho_i V_i = n_i$) we have:

[1] The derivation is done for the spherical particle liquid. The result for the non-spherical particles is the same

$$-P_i = \frac{\partial F_V}{\partial V_i} = -\frac{n_i}{v_i}kT + \left.\frac{\delta \mathcal{F}^{exc}}{\delta \rho}\right|_{\rho_0} \rho_0 + \frac{kT}{2}\rho_0^2 c(k=0) - \left.\frac{\delta \mathcal{F}^{exc}}{\delta \rho}\right|_{\rho_0} \rho_0 - \frac{kT}{2}\sum_i (-\rho_0)\int_V \Delta c(i2)\Delta\rho(2)d2 \tag{37}$$

This gives:

$$P_i V_i = n_i kT - \frac{kT}{2}\rho_0^2 c(k=0)V_i - \frac{kT}{2}\sum_i \rho_0 V_i \int_V \Delta c(i2)\Delta\rho(2)d2 \tag{38}$$

Taking a sum of $P_i V_i$, and considering that $\sum_i X_i V_i = \int_V X(1)d1$ we get the following:

$$\int_V P(1)d1 = NkT - \frac{kT}{2}\rho_0^2 c(k=0)V - \frac{kT}{2}\rho_0 \int_V d1 \int_V c(12)\Delta\rho(2)d2 \tag{39}$$

The last term can be rewritten as follows:

$$\frac{kT}{2}\rho_0 \int_V d1 \int_V c(12)\Delta\rho(2)d2 = \frac{kT}{2}\rho_0 \int_V d2\Delta\rho(2)\int_V c(12)d1 = \tag{40}$$

$$\frac{kT}{2}\rho_0 c(k=0)\int_V \Delta\rho(2)d2 = -\frac{kT}{2}\rho_0 c(k=0)\Delta N = -\frac{kT}{2}\rho_0^2 c(k=0)\Delta V \tag{41}$$

This gives the final results:

$$\int_V P(1)d1 = NkT - \frac{kT}{2}c(k=0)\rho_0^2(V-\Delta V) \tag{42}$$

5 Mechanical work of the solvent in the solvation process

In the paper we consider the solvation process which includes three states: state 0 with the volume $V - \Delta V$ and number of particles N, state 1 with the volume V and number of particles $N + \Delta N$ (with the same density, e.g. $N/(V-\Delta V) = (N+\Delta N)/V$, and the last state, with box of volume V with N particles and one solute molecule (where ΔV is the partial molar volume of the solute). Using the formulae derived in the previous sections we can calculate the mechanical works W_{01} and W_{12} of the system in transitions from state 0 to state 1 and from state 1 to state 2. The pressure in state 0 is

$$P_0 = n_0 kT - \frac{kT}{2}n_0^2 \hat{c}_S(k=0) \tag{43}$$

The pressure contribution in the inhomogeneous state 2 was found in the previous section:

$$\int_V P(\mathbf{r})d\mathbf{r} = NkT - \frac{kT}{2}\hat{c}_S(k=0)n_0^2(V-\Delta V) \tag{44}$$

Using this we find, that works $W_{01} = -P_0\Delta V$ and $W_{12} = P_0 V - \int_V P_2(\mathbf{r})d\mathbf{r}$ compensate each other:

$$W_{01} = -W_{12} = n_0 kT\Delta V - \frac{kT}{2}n_0^2\hat{c}(k=0)\Delta V \tag{45}$$

So, total mechanical work of the solvent is zero, and the change of the Gibbs free energy is equivalent tot the change of the Helmholtz free energy:

$$\Delta G_{solv} = \Delta F_{01} + \Delta F_{12} = \Delta\Theta_{MDFT} - n_0 kT\Delta V + \frac{kT}{2}n_0^2\hat{c}(k=0)\Delta V \tag{46}$$

6 Energy components in different states

	State 0: Uniform box(N,$V-\Delta V$)	State 1: Uniform box($N+\Delta N$,V)	State 2: Box(N,V) + Solute
F^{id}	$NkT\ln\Lambda^3\Lambda_{rot}\rho_0 - NkT$	$(N+\Delta N)kT\ln\Lambda^3\Lambda_{rot}\rho_0 - (N+\Delta N)kT$	$(N+\Delta N)kT\ln\Lambda^3\Lambda_{rot}\rho_0 - (N+\Delta N)kT$ $+\Delta\Theta^{id}_{MDFT} + kT\ln\Lambda^3\Lambda_{rot}\rho_0\int\Delta\rho(1)d1$
F^{exc}	$\frac{\delta\mathcal{F}^{exc}}{\delta\rho}N + \frac{kT}{2}n_0^2\hat{c}(k=0)(V-\Delta V)$	$\frac{\delta\mathcal{F}^{exc}}{\delta\rho}(N+\Delta N) + \frac{kT}{2}n_0^2\hat{c}(k=0)V$	$\frac{\delta\mathcal{F}^{exc}}{\delta\rho}(N+\Delta N) + \frac{kT}{2}n_0^2\hat{c}(k=0)V$ $+\Delta\Theta^{exc}_{MDFT} + \frac{\delta\mathcal{F}^{exc}}{\delta\rho}\int\Delta\rho(1)d1$
PV	$n_0kT(V-\Delta V)$ $-\frac{kT}{2}n_0^2c(k=0)(V-\Delta V)$	$n_0kTV - \frac{kT}{2}n_0^2c(k=0)V$	$NkT - \frac{kT}{2}n_0^2c(k=0)(V-\Delta V)$
G	$NkT\ln\Lambda^3\Lambda_{rot}\rho_0 + \frac{\delta\mathcal{F}^{exc}}{\delta\rho}N$	$(N+\Delta N)kT\ln\Lambda^3\Lambda_{rot}\rho_0+$ $\frac{\delta\mathcal{F}^{exc}}{\delta\rho}(N+\Delta N)$	$NkT\ln\Lambda^3\Lambda_{rot}\rho_0+$ $\frac{\delta\mathcal{F}^{exc}}{\delta\rho}N + \frac{kT}{2}n_0^2\hat{c}(k=0)\Delta V - \Delta NkT$ $+\Delta\Theta_{MDFT}$

Note: Here we use that $\int\Delta\rho = -\Delta N$, and $n_0 = N/(V-\Delta V) = (N+\Delta N)/V$. For more detailed description of the states see Figure 1 in the paper.

Using the table we can find the change in the Gibbs free energy in the solvation process:

$$\Delta G = G^{state2} - G^{state0} = \Delta\Theta_{MDFT} + \frac{kT}{2}n_0^2\hat{c}(k=0)\Delta V - \Delta NkT \tag{47}$$

7 Chemical potential of a non-fixed solute

We obtained the free energy expression for the solution of solute constrained to be at fixed position. However, in experiments and in MD simulations solutes are usually not constrained. This does not affect the excess free energy, but have an effect on the ideal chemical potential of solvent. To show it we write the free energy expression for the final state [2] :

$$F_2 = NkT \ln \Lambda^3 \frac{N+\Delta N}{N} - (N+\Delta N)kT + \left.\frac{\delta \mathcal{F}}{\delta \rho}\right|_{\rho_0} \cdot N + \frac{kT}{2}\rho_0^2 c(k=0)V + \Delta\Theta_{MDFT} \tag{48}$$

There is N solvent particles in the system of volume V. If we let them move over all the volume, this will result is a following chemical potential of the solvent:

$$\mu_2 = \left.\frac{\delta \mathcal{F}}{\delta \rho}\right|_{\rho_0} + kT \ln \frac{N}{V} \tag{49}$$

We can find this expression by taking derivative of (48) over N. To do it, we first use the equality $-\Delta N kT \approx -NkT \ln (N+\Delta N)/N$ to get rid of ΔN in (48):

$$F_2 \approx kT \ln \Lambda^3 \frac{N+\Delta N}{V} - NkT \ln \frac{N+\Delta N}{V} - NkT \tag{50}$$

$$+ \left.\frac{\delta \mathcal{F}}{\delta \rho}\right|_{\rho_0} \cdot N + \frac{kT}{2}\rho_0^2 c(k=0)V + \Delta\Theta_{MDFT} \tag{51}$$

Taking derivative over N we find:

$$\mu_2 \approx kT \ln \Lambda^3 \frac{N}{V} + \left.\frac{\delta \mathcal{F}}{\delta \rho}\right|_{\rho_0} + \frac{\partial \Delta\Theta}{\partial N} \tag{52}$$

We assume, that solvation of solute and solvent molecule is independent, which means $\partial\Delta\Theta/\partial N = 0$. This gives the expression (49)

For the homogeneous fluid the following relation is true:

$$G = \sum_i \mu_i N_i \tag{53}$$

where summation is done over all components of solution. In our case we can use the expression for the Gibbs free energy of the final state:

$$\mu_2 N + \mu_{solute} = F_2 + \int_V P dr = NkT \ln \Lambda^3 \frac{N}{V} - NkT + \left.\frac{\delta \mathcal{F}}{\delta \rho}\right|_{\rho_0} \cdot N + \frac{kT}{2}\rho_0^2 c(k=0)\Delta V + \Delta\Theta_{MDFT} \tag{54}$$

Taking into account (49) and canceling $\mu_2 N$ we get the following expression for the chemical potential of the solute:

$$\mu_{solute} = \Delta\Theta_{MDFT} + \frac{kT}{2}\rho_0^2 c(k=0)\Delta V \tag{55}$$

[2] For the sake of simplicity derivation is done for the fluid of spherical particles. This does not affect the form of the final result. In the case of non-spherical rigid particles the final result is the same.

8 Equivalence of the free energy calculation in 3DRISM and MDFT

In the MDFT theory the free energy is calculated as the minimal value of expression (9). In the 3DRISM-HNC theory the solvation free energy is calculated using the following formula:

$$\mathcal{F}_{HNC} = \sum_{\alpha}^{N_{sites}} n_0 kT \int \left(\frac{h_\alpha(\mathbf{r})^2}{2} - \frac{h_\alpha(\mathbf{r}) c_\alpha(\mathbf{r})}{2} - c_\alpha(\mathbf{r}) \right) d\mathbf{r} \tag{56}$$

where $h_\alpha(\mathbf{r})$, $c_\alpha(\mathbf{r})$ are the solute site-solvent correlation functions.

We show, that for the one-site (spherical) solvent these formulae are equivalent. In that case we have only one kind of solute site functions. We define them as h_0, c_0 (to distinguish from solvent functions). We express the density at point $\mathbf{r}$ as $n(\mathbf{r}) = n_0 h_0(\mathbf{r})$. Subtituting this into the free-energy functional used in the MDFT calculations we have

$$\begin{aligned} F = kTn_0 \int g_0(\mathbf{r}) \ln g_0(\mathbf{r}) d\mathbf{r} - kTn_0 \int h_0(\mathbf{r}) d\mathbf{r} + n_0 \int g_0(\mathbf{r}) U(\mathbf{r}) d\mathbf{r} \\ -\frac{kT}{2} n_0^2 \iint h_0(\mathbf{r}_{01}) c(r_{12}) h_0(\mathbf{r}_{02}) d\mathbf{r_1} d\mathbf{r_2} \end{aligned} \tag{57}$$

where 0 is the solute position. We rewrite this as

$$F = F^{id} + F^{exc} \tag{58}$$

where

$$F^{id} = kTn_0 \int \left(g_0(\mathbf{r}) \ln g_0(\mathbf{r}) - h_0(\mathbf{r}) + \beta g_0(\mathbf{r}) U(\mathbf{r}) \right) d\mathbf{r} \tag{59}$$

$$F^{exc} = -\frac{kT}{2} n_0^2 \iint h_0(\mathbf{r}_{01}) c(r_{12}) h_0(\mathbf{r}_{02}) d\mathbf{r}_1 d\mathbf{r}_2 \tag{60}$$

Using the OZ relation we obtain the following:

$$F^{exc} = -\frac{n_0 kT}{2} \int (h_0(\mathbf{r}_{02}) - c_0(\mathbf{r}_{02})) h_0(\mathbf{r}_{02}) d\mathbf{r}_2 = n_0 kT \int \left(-\frac{h_0(\mathbf{r})^2}{2} + \frac{h_0(\mathbf{r}) c_0(\mathbf{r})}{2} \right) d\mathbf{r} \tag{61}$$

Using the HNC closure relation

$$g_0(\mathbf{r}) = e^{-\beta U(\mathbf{r}) + h_0(\mathbf{r}) - c_0(\mathbf{r})} \tag{62}$$

we have:

$$F^{id} = n_0 kT \int \Big(g_0(\mathbf{r}) \big(-\beta U(\mathbf{r}) + h_0(\mathbf{r}) - c_0(\mathbf{r}) \big) - h_0(\mathbf{r}) + \beta g_0(\mathbf{r}) U(\mathbf{r}) \Big) d\mathbf{r} \tag{63}$$

Opening the brackets and cancelling the $\beta g_0(\mathbf{r}) U(\mathbf{r}) d\mathbf{r}$ we obtain the following expression:

$$F^{id} = n_0 kT \int \Big(\big(g_0(\mathbf{r}) - 1 \big) h_0(\mathbf{r}) - g_0(\mathbf{r}) c_0(\mathbf{r}) \Big) d\mathbf{r} \tag{64}$$

Using that $g_0(\mathbf{r}) = h_0(\mathbf{r}) + 1$

$$F^{id} = n_0 kT \int \Big(h_0(\mathbf{r})^2 - h_0(\mathbf{r}) c_0(\mathbf{r}) - c_0(\mathbf{r}) \Big) d\mathbf{r} \tag{65}$$

Adding F^{id} and F^{exc}:

$$F = n_0 kT \int \left(\frac{h_0(\mathbf{r})^2}{2} - \frac{h_0(\mathbf{r}) c_0(\mathbf{r})}{2} - c_0(\mathbf{r}) \right) d\mathbf{r} \tag{66}$$

This is the 3DRISM solvation free energy expression for a one-site solvent. Equivalence is proven in that case.

9 Comparison of MDFT NPT and μVT results to the experimental ones

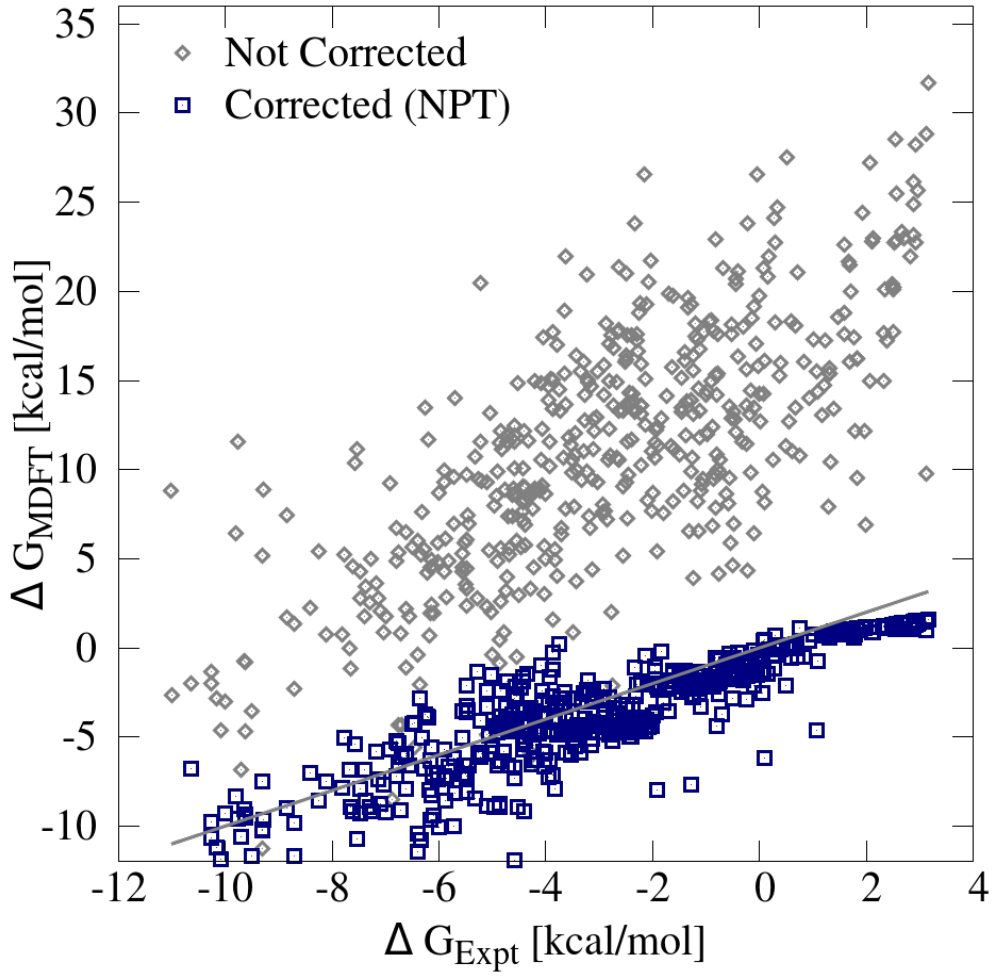

Figure 1: Results of the MDFT calculations in μVT (not corrected) and NPT (corrected) ensembles versus the experimental ones.

	μVT	NPT
Mean Error	13.88736	-0.77477
σ	5.34291	1.61535
RMSD	14.87970	1.79154

Table 1: Errors of the MDFT calculations in μVT (not corrected) and NPT (corrected) ensembles with respect to the experimental results. (Values are in kcal/mol)

10 Comparison of the theoretical and empirical corrections

In the work Palmer et al. Journal of Physics: Condensed Matter 22, 492101 (2010) empirical Universal Corection (UC) method of solvation free energy calculations is described. It is based on the 3DRISM calculations corrected by the partial molar volume with the molecule. The model is described by the formula:

$$\Delta G_{UC} = a\Delta G_{3DRISM}\rho_0\Delta V + b \tag{67}$$

where ΔG_{3DRISM} is a free energy, calculated with 3DRISM, ρ is a water density, ΔV is partial molar volume of the molecule, a and b are empirical coefficients obtained by fitting. The following values for a and b are reported by Palmer et al.: a = -3.312 kcal/mol, b = 1.152 kcal/mol. As we can see, UC-model is similar in form to the ensemble correction formula, reported in the current paper, which for the case of 3DRISM calculation can be written in a following way:

$$\Delta G_{NPT} = \Delta G_{3DRISM} + a_{theor}\rho_0\Delta V \tag{68}$$

where $a_{theor} = \frac{1}{2}\rho_0\hat{c}(k=0)$. So, we can compare the coefficient in the theoretical and empirical models. We note, that the coefficient a_{theor} depends on the water c-function, that's why in our comparison we use the same c-function which was used in the Palmer's calculations. In that case we obtain a_{theor} = -3.26 kcal/mol, which is close to the value reported by Palmer et. al. We note, although, that in their calculations the RMSD error is smaller, which indicates that some contributions to the partial molar volume correction are still need to be identified.

11 Test of the numerical errors associated with grid discretization

To be sure in the accuracy of the presented results we need to check that the numerical errors associated with the finite grid size are smaller than the errors obtained after the ensemble correction. To demonstrate this we can choose one molecule and show that the free energy weekly depends on the orientation of the molecule. It is known, that the most problematic for the DFT theory are the molecule with high partial atomic charges. That's why for our investigation we have chosen 2-chloro-111-trimethoxyethane (see Figure 2). This molecule has quite high partial charges on three oxygen atoms (-0.44) and on the central carbon atom (0.52) (see Table 2). For this molecule 3DRISM and MDFT calculations were performed. In the 3DRISM calculations two different grids were used: one with grid-size 0.5 Åand another with grid-size 0.2 Å. Buffer in both cases was 15 Å. The results of the calculations for 0.5 Åand 0.2 Åare shown in Tables 3 and 4 respectively. We see, that for the grid with step 0.5 Ådifference in energies at different rotations

Atom	Group	Partial charge
C	CH_3	0.1313
C	CH_2Cl	0.0066
C	C-CO_3	0.522
O	C-O-C	-0.4397
Cl	CH_2Cl	-0.1443
H	CH_3	0.0422
H	CH_2Cl	0.0803

Table 2: Partial charges of the 2-chloro-111-trimethoxyethane

can vary in a range of 1 kcal/mol, which is about the same in a magnitude than the accuracy of predictions themselves. For the grid with step 0.2 Åmaximal difference in energies in different rotations is 0.43 kcal/mol for non-corrected and 0.28 kcal/mol for correct values, while maximal standard deviations are 0.181 and 0.117 kcal/mol respectively. This is still a large, but already acceptable level of numerical errors, as it is 2-3 times lower than the accuracy of the predictions. In our calculations we used the grid with grid step of 0.2 Å.

For the MDFT calculations the only grid was used with grid step 0.5 Åin spatial direction, and 6x4 different rotations at each spatial point. The results are presented in Table 5 We see that the maximal difference in solvation energies is 0.35 kcal/mol (0.14 kcal/mol after the ensemble correction), which is an acceptable accuracy. Also, we need to mention, that for the less charged molecules, such as undecan-2-one, the errors are yet smaller (see Table 6) This justifies using this grid in the MDFT calculations.

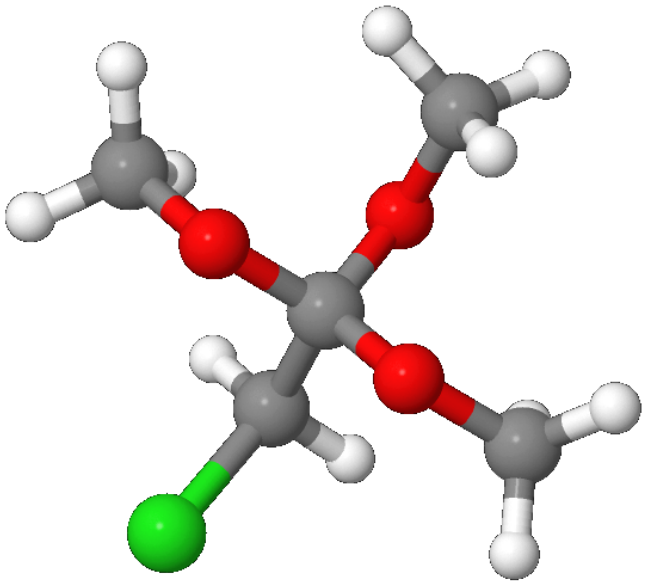

Figure 2: 2-chloro-111-trimethoxyethane used for the numerical accuracy investigation. Hydrogen, Carbon, Oxygen and Clorine atoms are shown in white, gray, red and green respectively

Angle	Rotation over Oy		Rotation over Oz	
	μVT	NPT	μVT	NPT
72^o	12.995	-5.180	13.536	-4.808
144^o	13.022	-5.177	13.051	-5.133
216^o	13.751	-4.678	14.074	-4.432
288^o	12.876	-5.225	13.800	-4.582
max-min	0.875	0.547	1.024	0.701
Std	0.398	0.259	0.436	0.305

Table 3: Results of the 3DRISM free energy calculations for 2-chloro-111-trimethoxyethane in different rotations for the grid with step of 0.5 Å. All values are in kcal/mol.

Angle	Rotation over Oy		Rotation over Oz	
	μVT	NPT	μVT	NPT
72^o	13.413	-4.877	13.518	-4.818
144^o	13.534	-4.773	13.505	-4.819
216^o	13.842	-4.595	13.454	-4.841
288^o	13.598	-4.769	13.614	-4.764
max-min	0.429	0.282	0.160	0.077
Std	0.181	0.117	0.067	0.033

Table 4: Results of the 3DRISM free energy calculations for 2-chloro-111-trimethoxyethane in different rotations for the grid with step of 0.2 Å. All values are in kcal/mol.

Angle	Rotation over Oy		Rotation over Oz	
	μVT	NPT	μVT	NPT
0^o	10.099	-7.395	10.099	-7.395
72^o	9.836	-7.501	9.955	-7.489
144^o	9.749	-7.506	10.002	-7.471
216^o	9.799	-7.536	10.042	-7.407
288^o	10.039	-7.415	9.980	-7.415
max-min	0.350	0.141	0.144	0.094
Std	0.155	0.062	0.056	0.042

Table 5: Results of the MDFT free energy calculations for 2-chloro-111-trimethoxyethane in different rotations for the grid with step of 0.5 Å. All values are in kcal/mol.

12 Calculations of polar/nonpolar components with different water models

To check how the results change if we use different $\hat{c}_S(k)$ functions, we performed additional MDFT calculations for all molecules with three different $\hat{c}_S(k)$ functions, which we refer here as SPCE, TIP3P, and RISM . The first two correspond to the functions that are obtained from the MD simulation of SPCE or TIP3P water (and are related to the structure factor of water in these models). RISM refers to the function that is obtained from a 1D-RISM calculation with TIP3P

Angle	Rotation over Oy		Rotation over Oz	
	μVT	NPT	μVT	NPT
0^o	26.558	-4.192	26.558	-4.192
72^o	26.501	-4.234	26.570	-4.235
144^o	26.682	-4.137	26.627	-4.190
216^o	26.577	-4.176	26.624	-4.177
288^o	26.681	-4.165	26.712	-4.147
max-min	0.181	0.096	0.154	0.088
Std	0.080	0.036	0.061	0.032

Table 6: Results of the MDFT free energy calculations for undecan-2-one in different rotations for the grid with step of 0.5 Å. All values are in kcal/mol.

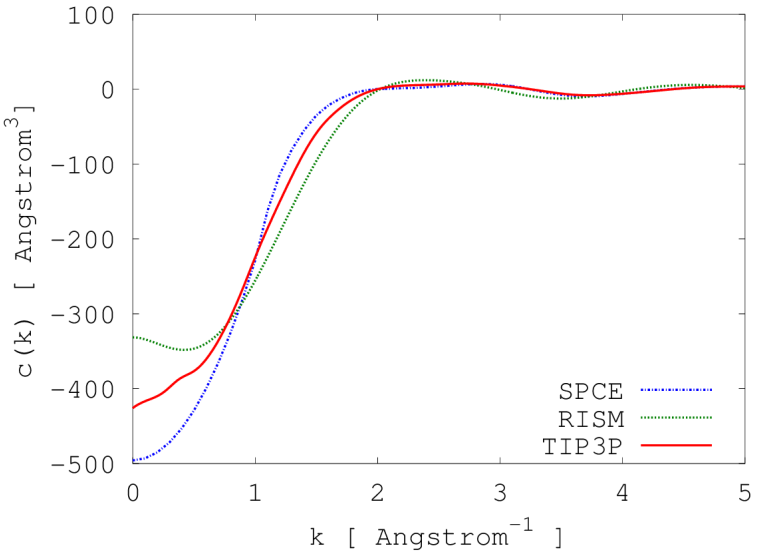

Figure 3: Different $\hat{c}_S(k)$ functions used for calculations.

water. These $c_S(k)$ functions are presented in Figure 3 With each of these three $c_S(k)$ functions nonpolar, polar and total solvation free energies were calculated. The results are in Figures 4, 5, 7. The statistical results are summarized in Table 8. We see, that all three models give a satisfactory correlation with MD simulations results. The σ values and correlation coefficient are almost the same for SPCE and RISM waters. We see, that the main contribution to the errors is a systematic shift (M), which depends much on the choice of $\hat{c}_S(k)$. However, there are almost no shifts for polar component, which is difference between the total and nonpolar parts. This means, that the main source of errors is in the incorrect treatment of nonpolar interactions, which cancels out if we subtract the nonpolar part from the total energy.

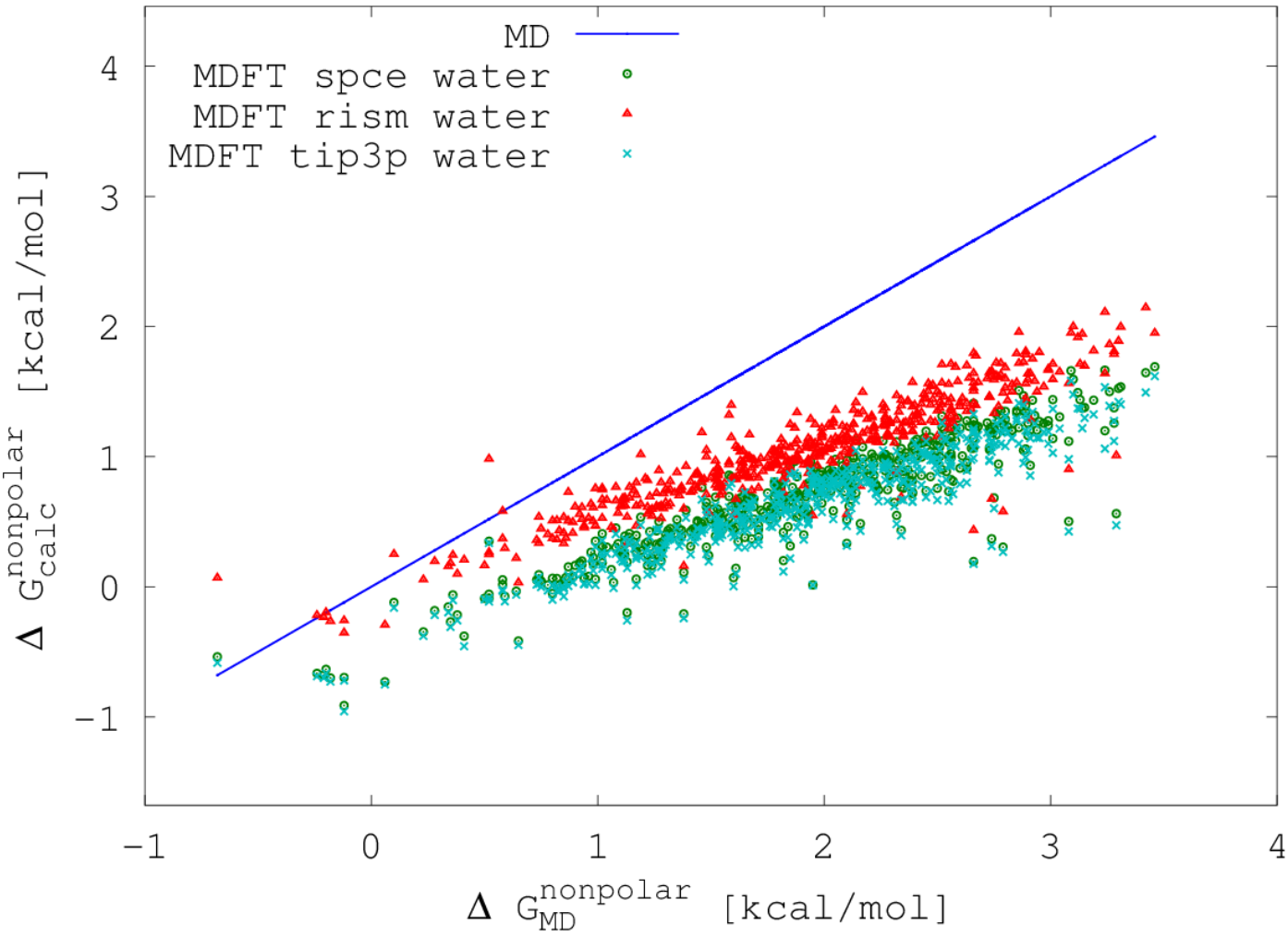

Figure 4: Nonpolar component

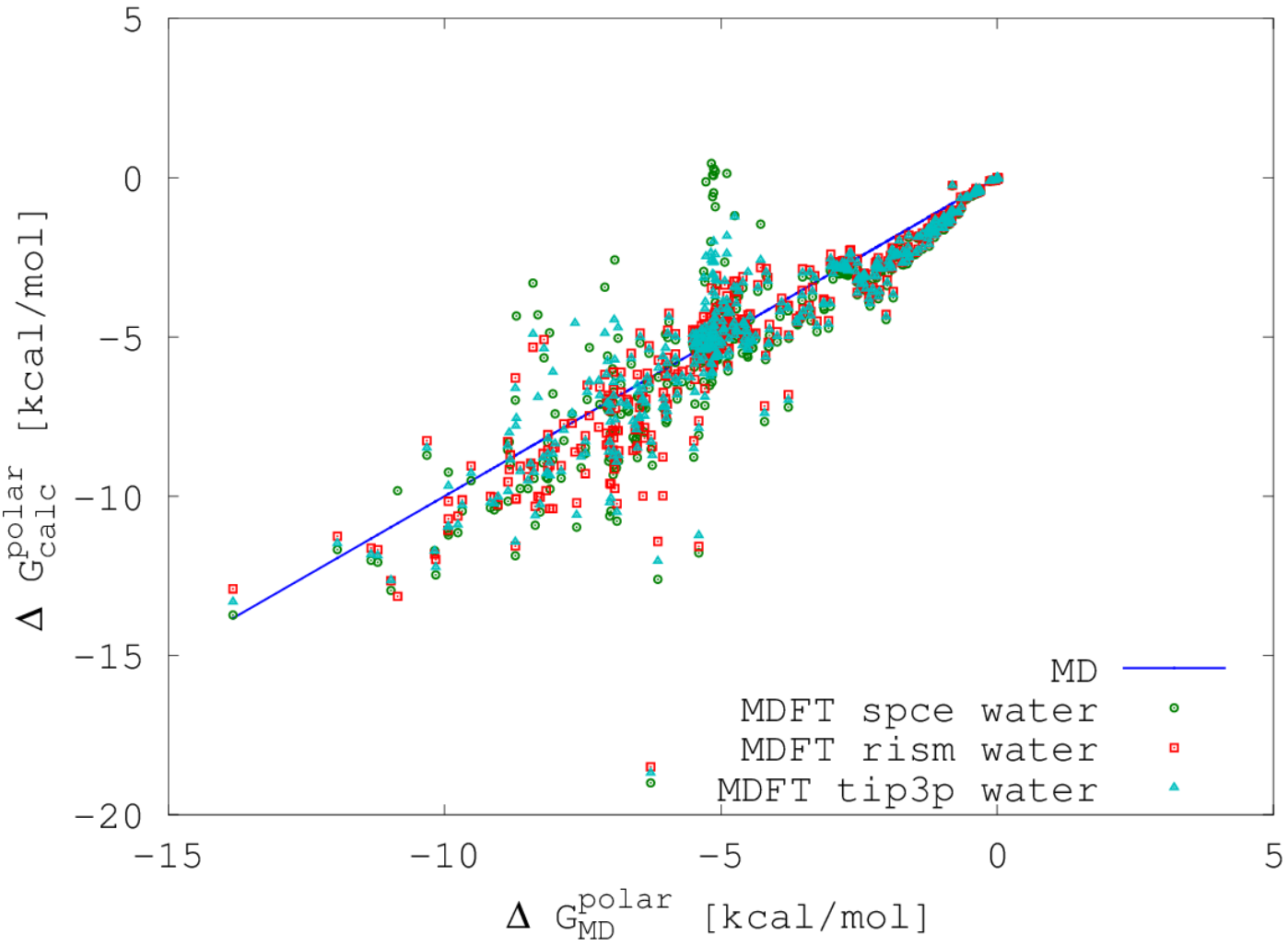

Figure 5: Polar component

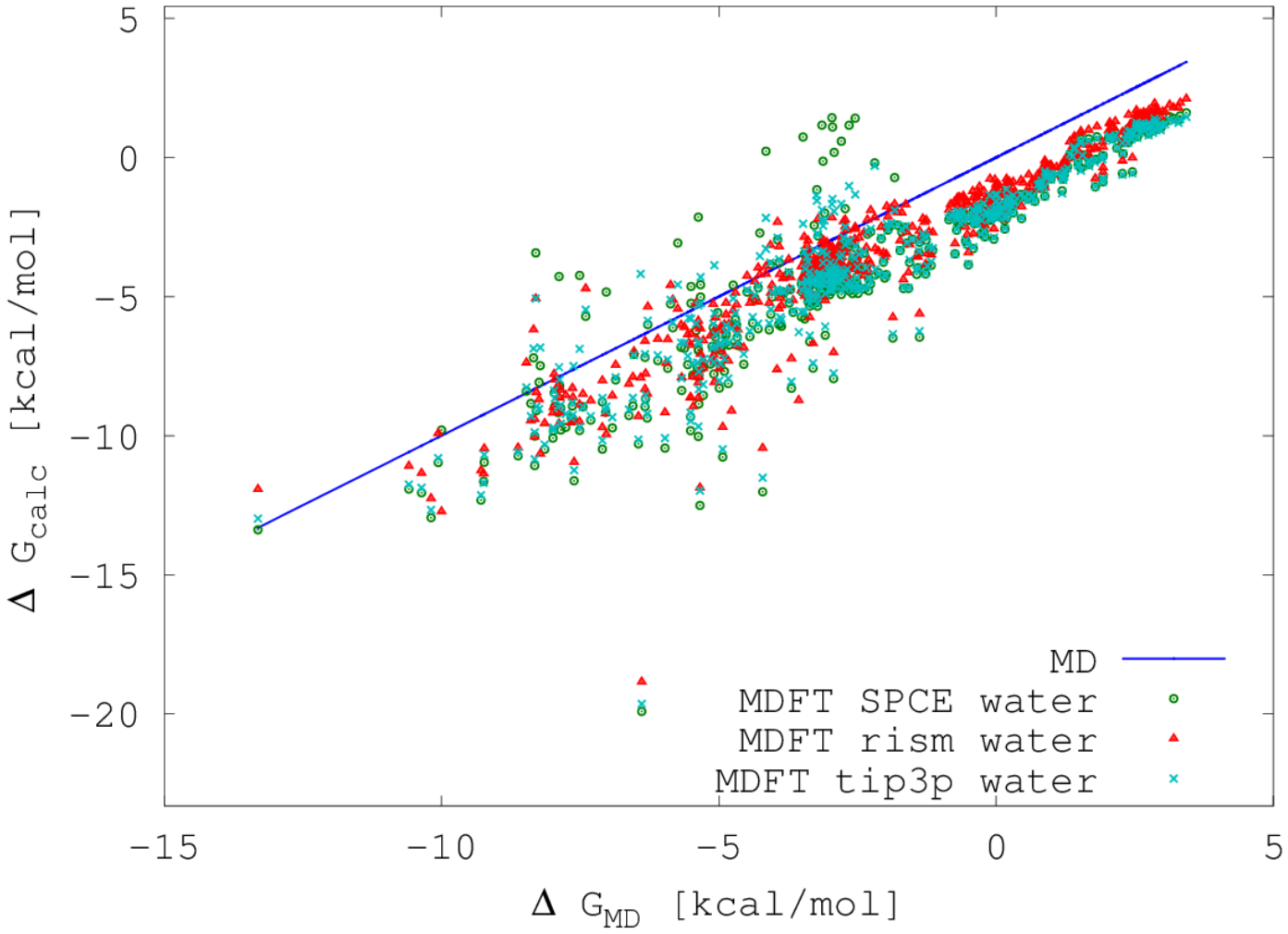

Figure 6: Total solvation free energy with respect to MD simulations

Error	SPCE	RISM	TIP3P
Nonpolar			
RMSD	1.261	0.927	1.325
σ	0.357	0.362	0.370
M	-1.209	-0.853	-1.273
r	0.922	0.922	0.917
$N_{converged}$	504	504	504
Polar			
RMSD	1.482	1.125	1.208
σ	1.454	1.072	1.186
M	-0.283	-0.340	-0.231
r	0.880	0.935	0.914
$N_{converged}$	488	503	496
Total			
RMSD	2.109	1.615	1.942
σ	1.482	1.084	1.221
M	-1.501	-1.197	-1.510
r	0.898	0.944	0.926
$N_{convergred}$	488	503	496

Table 7: Errors of MDFT calculations with different water models (with respect to MD calculations)

Error	SPCE	RISM	TIP3P	MD
RMSD	2.032	1.504	1.825	1.259
σ	1.849	1.410	1.622	1.062
M	-0.842	-0.524	-0.837	0.676
r	0.836	0.903	0.866	0.943
N	488	503	496	504

Table 8: Errors of MDFT calculations with different water models (with respect to experimental data)

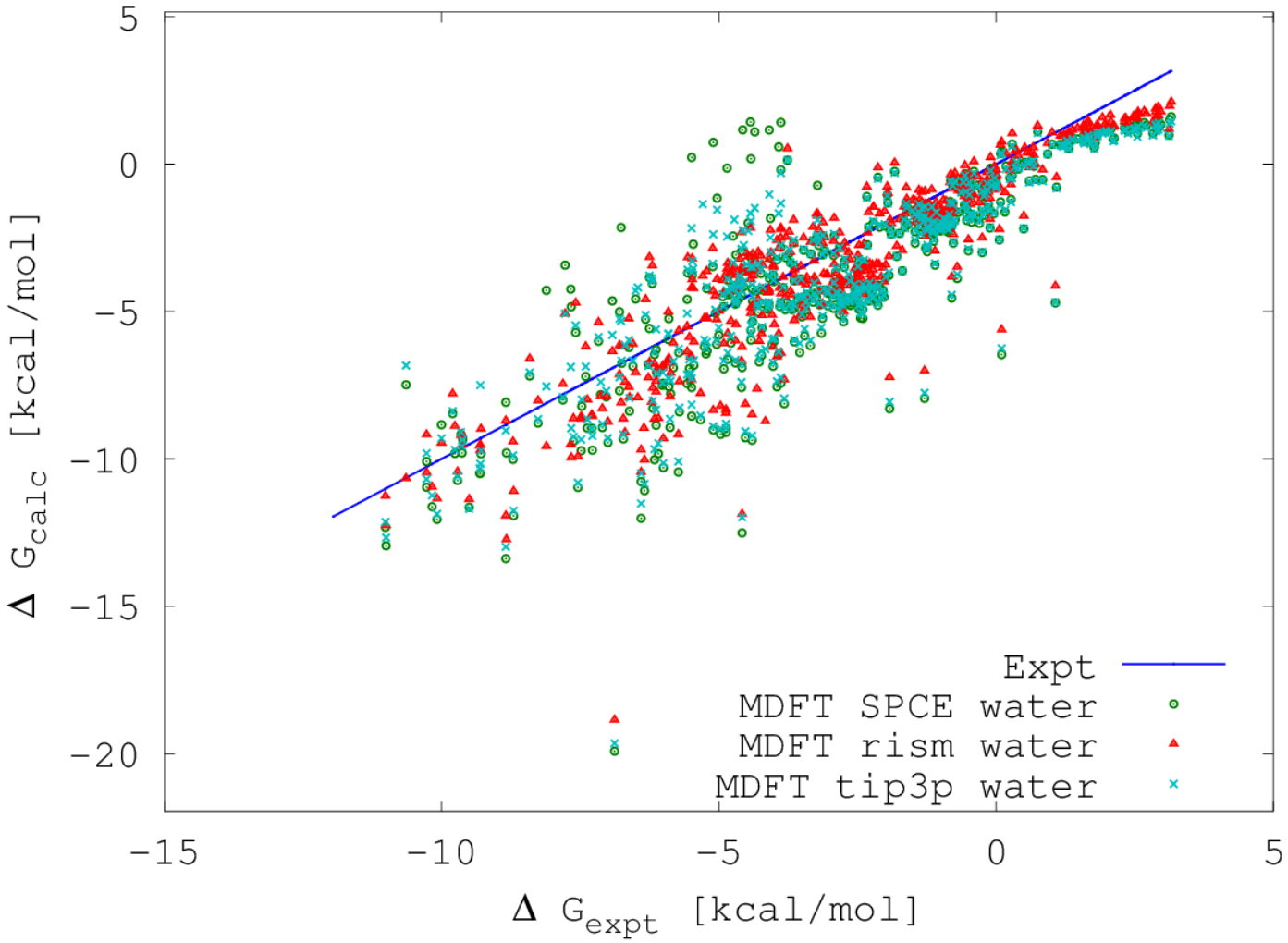

Figure 7: Total solvation free energy with respect to experiment

13 List of compounds used in the calculations

Table 9: Compounds in used for the calculations and their free energies calculated by different methods. Values are given in kcal/mol. MD data and experimental free energies are taken from Mobley et al. J. Chem. Theory Comput., 2009, 5, 350–358.

Compound	$\Delta\Theta^{\mu VT}_{MDFT}$	$\Delta\Theta^{\mu VT}_{3DRISM}$	ΔG^{NPT}_{MDFT}	ΔG^{NPT}_{3DRISM}	ΔG_{MD}	ΔG_{expt}
1112-tetrachloroethane	13.878	16.191	-1.717	1.458	0.110	-1.280
111-trichloroethane	13.122	14.865	-0.922	1.640	0.750	-0.190
111-trifluoro-222-trimethoxyethane	14.170	-	-4.358	-	-2.260	-0.800
111-trifluoropropan-2-ol	-6.488	6.253	-6.278	-5.833	-3.560	-4.160
111-trimethoxyethane	10.074	12.833	-5.678	-4.033	-3.890	-4.420
1122-tetrachloroethane	11.567	14.873	-3.164	0.413	-0.410	-2.470
112-trichloro-122-trifluoroethane	17.433	18.651	0.583	3.349	1.530	1.770
112-trichloroethane	8.690	11.955	-3.777	-0.730	-0.500	-1.990
11-diacetoxyethane	7.997	-	-8.901	-	-7.900	-4.970
11-dichloroethane	9.758	12.021	-1.653	0.694	0.170	-0.840
11-dichloroethene	10.549	12.253	-0.455	1.544	1.240	0.250
11-diethoxyethane	14.176	16.187	-3.948	-2.175	-2.180	-3.280
11-difluoroethane	6.420	9.200	-2.109	-0.127	0.190	-0.110
1234-tetrachlorobenzene	19.097	21.152	-1.726	2.027	-0.320	-1.340
1235-tetrachlorobenzene	19.775	21.877	-1.255	2.625	-0.020	-1.620
123-trichlorobenzene	16.411	18.638	-2.069	1.190	-0.380	-1.240
123-trimethylbenzene	17.463	19.807	-2.082	0.874	-0.650	-1.210
1245-tetrachlorobenzene	19.631	21.700	-1.409	2.540	0.250	-1.340
124-trichlorobenzene	16.754	19.192	-1.877	1.694	-0.180	-1.120
124-trimethylbenzene	17.770	20.251	-1.978	1.049	-0.360	-0.860
12-diacetoxyethane	5.220	9.446	-10.778	-8.423	-8.320	-6.340
12-dibromoethane	13.266	15.086	-1.082	1.656	0.190	-2.330
12-dichlorobenzene	13.816	16.260	-2.298	0.534	-0.640	-1.360
12-dichloroethane	7.545	10.445	-3.073	-0.584	-0.520	-1.790
12-dichloropropane	10.658	13.554	-2.789	0.086	-0.200	-1.270
12-diethoxyethane	11.372	13.859	-5.998	-4.265	-3.080	-3.540
12-dimethoxyethane	5.592	8.142	-6.350	-5.385	-3.360	-4.840
12-ethanediol	-12.731	-	-7.519	-	-7.620	-9.300
135-trichlorobenzene	17.620	19.852	-1.257	2.301	0.450	-0.780
135-trimethylbenzene	18.372	20.848	-1.804	1.222	0.040	-0.900
13-dichlorobenzene	14.439	16.851	-1.927	1.090	0.010	-0.980
13-dichloropropane	11.331	13.901	-2.328	0.440	-0.380	-1.890
13-dimethylnaphthalene	17.547	20.801	-4.684	-1.184	-2.790	-2.470
14-dichlorobenzene	14.180	16.886	-2.181	1.095	-0.100	-1.010
14-dichlorobutane	13.337	16.178	-2.690	0.552	-0.270	-2.320
14-dimethyl-piperazine	10.371	10.905	-5.400	-5.466	-7.400	-7.580
14-dimethylnaphthalene	17.066	20.292	-4.858	-1.361	-3.290	-2.820
14-dioxane	5.476	7.871	-4.898	-3.458	-4.350	-5.060
1-bromo-2-chloroethane	11.513	13.554	-1.281	1.283	0.020	-1.950

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Compound	$\Delta\Theta^{\mu VT}_{MDFT}$	$\Delta\Theta^{\mu VT}_{3DRISM}$	ΔG^{NPT}_{MDFT}	ΔG^{NPT}_{3DRISM}	ΔG_{MD}	ΔG_{expt}
1-bromo-2-methylpropane	15.782	17.613	-0.396	2.464	1.240	-0.030
1-bromobutane	16.338	18.419	-0.242	2.725	1.680	-0.400
1-bromoheptane	24.687	27.319	-0.021	4.582	1.660	0.340
1-bromohexane	21.948	24.436	-0.069	4.007	1.780	0.180
1-bromooctane	27.528	30.362	0.052	5.218	1.920	0.520
1-bromopentane	19.134	21.434	-0.141	3.360	1.480	-0.100
1-bromopropane	13.552	15.392	-0.326	2.102	1.290	-0.560
1-chloro-222-trifluoroethane	8.760	11.901	-2.508	0.235	0.160	0.060
1-chlorobutane	14.427	16.714	-0.590	2.230	0.990	-0.160
1-chloroheptane	22.745	25.696	-0.375	4.136	1.530	0.290
1-chlorohexane	19.738	22.438	-0.598	3.271	1.230	0.000
1-chloropentane	17.061	19.500	-0.648	2.664	1.180	-0.070
1-chloropropane	11.593	13.630	-0.694	1.634	0.920	-0.330
1-ethylnaphthalene	17.523	20.644	-4.664	-1.275	-3.000	-2.400
1-iodobutane	15.649	17.954	-1.468	1.600	0.580	-0.250
1-iodoheptane	24.099	27.127	-1.185	3.687	1.190	0.270
1-iodohexane	21.305	24.165	-1.274	3.013	0.660	0.080
1-iodopentane	18.497	21.187	-1.339	2.392	0.660	-0.140
1-iodopropane	12.897	15.026	-1.530	1.054	0.000	-0.530
1-methyl-imidazole	2.250	5.243	-7.029	-5.926	-6.330	-8.410
1-methyl-pyrrole	7.680	9.856	-3.483	-2.311	-2.590	-2.890
1-methylcyclohexene	18.055	19.772	0.186	3.112	1.330	0.670
1-methylnaphthalene	14.290	17.767	-4.969	-1.812	-3.240	-2.440
1-naphthol	-0.014	10.980	-6.851	-6.221	-7.510	-7.670
1-naphthylamine	4.991	11.823	-9.157	-5.829	-7.760	-7.280
1-nitrobutane	12.179	15.097	-2.878	0.228	-1.510	-3.090
1-nitropentane	14.995	18.047	-2.759	0.941	-1.290	-2.820
1-nitropropane	9.387	11.936	-2.987	-0.428	-1.380	-3.340
222-trifluoroethanol	-5.838	5.037	-4.749	-4.710	-3.950	-4.310
224-trimethylpentane	24.894	26.771	1.225	5.423	2.930	2.890
225-trimethylhexane	28.205	30.247	1.506	6.246	2.860	2.930
22-dimethylbutane	20.079	21.966	1.228	4.582	2.530	2.510
22-dimethylpentane	23.132	25.144	1.398	5.310	2.900	2.880
22-dimethylpropane	17.746	19.463	1.282	4.204	2.600	2.510
234-trimethylpentane	25.479	27.478	1.377	5.665	2.860	2.560
23-dimethylbuta-13-diene	15.987	18.081	-0.082	2.427	1.690	0.400
23-dimethylbutane	20.116	22.029	1.233	4.584	2.690	2.340
23-dimethylnaphthalene	17.534	20.653	-4.668	-1.295	-2.590	-2.780
23-dimethylpentane	22.725	24.646	1.254	5.083	2.660	2.520
23-dimethylphenol	4.500	12.321	-6.305	-4.060	-4.670	-6.160
23-dimethylpyridine	11.140	13.647	-4.263	-2.212	-3.270	-4.820
24-dimethylpentan-3-one	16.849	19.583	-3.391	-0.321	-2.470	-2.740
24-dimethylpentane	21.949	23.909	1.069	4.782	2.890	2.830
24-dimethylphenol	5.919	13.375	-7.011	-3.507	-4.550	-6.010
24-dimethylpyridine	11.490	13.952	-4.208	-2.197	-3.180	-4.860
25-dimethylphenol	9.941	14.687	-5.675	-2.399	-4.390	-5.910
25-dimethylpyridine	11.929	14.352	-3.985	-1.907	-2.830	-4.720
25-dimethyltetrahydrofuran	14.174	16.242	-2.299	-0.073	-1.890	-2.920

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Compound	$\Delta\Theta^{\mu VT}_{MDFT}$	$\Delta\Theta^{\mu VT}_{3DRISM}$	ΔG^{NPT}_{MDFT}	ΔG^{NPT}_{3DRISM}	ΔG_{MD}	ΔG_{expt}
26-dimethylaniline	9.324	14.006	-5.967	-3.228	-4.870	-5.210
26-dimethylnaphthalene	17.852	20.907	-4.568	-1.235	-2.650	-2.630
26-dimethylphenol	9.488	14.238	-5.898	-2.835	-4.090	-5.260
26-dimethylpyridine	11.554	13.588	-4.224	-2.526	-3.360	-4.590
2-bromo-2-methylpropane	16.065	17.937	-0.505	2.364	0.890	0.840
2-bromopropane	13.265	15.146	-0.569	1.897	0.970	-0.480
2-butoxyethanol	13.460	-	-3.708	-	-4.070	-6.250
2-chloro-111-trimethoxyethane	10.099	13.607	-7.321	-4.804	-3.300	-4.590
2-chloro-2-methylpropane	14.380	16.506	-0.757	1.984	0.820	1.090
2-chloroaniline	4.883	10.566	-6.626	-3.685	-4.960	-4.910
2-chlorobutane	14.248	16.393	-0.746	1.995	1.210	0.000
2-chlorophenol	6.008	12.125	-2.714	-1.971	-3.230	-4.550
2-chloropropane	11.456	13.587	-0.874	1.452	0.820	-0.250
2-chloropyridine	6.915	9.384	-5.211	-3.548	-3.360	-4.390
2-chlorotoluene	14.549	17.063	-2.141	0.677	-0.510	-1.140
2-ethoxyethanol	-4.305	3.517	-6.142	-9.227	-4.770	-6.690
2-ethylpyrazine	6.987	10.469	-6.598	-4.594	-5.680	-5.450
2-ethylpyridine	11.601	13.696	-4.140	-2.371	-3.210	-4.330
2-ethyltoluene	17.712	20.176	-1.971	1.068	-0.660	-1.040
2-fluorophenol	2.758	10.829	-1.340	-2.195	-3.240	-5.290
2-iodophenol	11.689	14.946	-3.906	-1.168	-2.910	-6.200
2-iodopropane	12.803	14.927	-1.672	0.918	0.290	-0.460
2-isobutylpyrazine	13.209	16.528	-5.896	-3.068	-5.100	-5.040
2-methoxy-111-trimethoxyethane	6.988	-	-10.015	-	-5.970	-5.730
2-methoxyaniline	4.549	10.385	-7.049	-5.286	-6.530	-6.120
2-methoxyethanamine	1.781	5.330	-6.626	-5.667	-5.620	-6.550
2-methoxyethanol	-4.308	2.986	-5.315	-7.699	-5.370	-6.760
2-methoxyphenol	4.289	-	-5.026	-	-4.740	-5.570
2-methyl-but-2-ene	15.405	17.273	0.585	2.964	2.380	1.310
2-methylbut-2-ene	15.405	17.273	0.585	2.964	2.280	1.310
2-methylbuta-13-diene	13.463	15.673	-0.010	2.239	1.810	0.680
2-methylbutan-1-ol	9.032	-	-3.438	-	-2.780	-4.420
2-methylbutan-2-ol	8.141	13.941	-1.631	-1.202	-2.960	-4.430
2-methylbutane	17.249	18.907	1.113	3.959	2.520	2.380
2-methylhexane	22.764	24.889	1.260	5.143	3.000	2.930
2-methylpent-1-ene	18.565	20.593	0.877	3.814	2.750	1.470
2-methylpentan-2-ol	11.559	16.830	-1.613	-0.791	-2.790	-3.920
2-methylpentan-3-ol	13.427	17.237	-0.238	-0.084	-2.190	-3.880
2-methylpentane	20.249	22.220	1.255	4.675	2.780	2.510
2-methylpropan-2-ol	5.660	10.694	-2.231	-2.083	-3.090	-4.470
2-methylpropane	14.973	16.553	1.193	3.623	2.740	2.320
2-methylpropene	13.035	14.869	0.695	2.768	2.340	1.160
2-methylpyrazine	3.580	7.156	-7.062	-5.464	-6.100	-5.510
2-methylpyridine	8.562	10.647	-4.398	-3.034	-3.410	-4.630
2-methyltetrahydrofuran	11.024	12.922	-2.524	-0.667	-1.950	-3.300
2-methylthiophene	11.925	13.932	-1.584	0.450	-0.220	-1.380
2-naphthol	0.760	10.515	-7.506	-6.694	-7.880	-8.110
2-naphthylamine	4.283	11.026	-7.929	-6.564	-7.870	-7.470

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Compound	$\Delta\Theta^{\mu VT}_{MDFT}$	$\Delta\Theta^{\mu VT}_{3DRISM}$	ΔG^{NPT}_{MDFT}	ΔG^{NPT}_{3DRISM}	ΔG_{MD}	ΔG_{expt}
2-nitroaniline	3.426	9.139	-8.597	-5.235	-7.960	-7.370
2-nitrophenol	-3.648	-	-11.942	-	-5.340	-4.580
2-nitropropane	9.469	11.867	-3.020	-0.544	-1.610	-3.130
2-nitrotoluene	11.780	14.741	-4.456	-1.543	-3.140	-3.580
2-phenylethanol	6.755	12.190	-5.195	-4.367	-5.330	-6.790
2-propoxyethanol	-0.382	-	-11.465	-	-4.210	-6.400
333-trimethoxypropionitrile	6.027	-	-10.418	-	-4.930	-6.400
33-dimethylbutan-2-one	12.795	15.450	-4.160	-1.579	-2.910	-3.110
33-dimethylpentane	22.870	24.772	1.339	5.147	2.530	2.560
34-dimethylphenol	5.662	-	-4.254	-	-5.330	-6.500
34-dimethylpyridine	11.561	14.063	-4.093	-1.952	-3.180	-5.220
35-dimethylphenol	5.542	-	-6.788	-	-5.120	-6.270
35-dimethylpyridine	12.146	14.498	-3.824	-1.730	-2.940	-4.840
3-acetylpyridine	5.425	8.981	-8.587	-6.453	-7.100	-8.260
3-chloroaniline	4.847	10.815	-6.638	-3.523	-5.370	-5.820
3-chloroprop-1-ene	9.562	11.973	-1.352	0.841	0.880	-0.570
3-chloropyridine	8.641	11.102	-3.884	-1.941	-2.500	-4.010
3-cyanophenol	-0.751	6.983	-9.057	-6.898	-7.040	-9.650
3-cyanopyridine	5.336	9.093	-6.620	-4.337	-4.660	-6.750
3-ethylpyridine	11.923	14.459	-3.965	-1.721	-2.960	-4.590
3-formylpyridine	2.046	5.816	-8.768	-7.324	-7.640	-7.100
3-hydroxybenzaldehyde	-3.571	-	-11.659	-	-9.240	-9.500
3-methoxyaniline	2.571	9.076	-8.922	-6.215	-7.450	-7.290
3-methoxyphenol	-1.167	-	-8.924	-	-7.030	-7.660
3-methyl-1h-indole	6.152	10.920	-8.580	-6.166	-6.550	-5.880
3-methyl-but-1-ene	16.202	18.023	1.020	3.532	2.800	1.830
3-methylbut-1-ene	16.202	18.023	1.020	3.532	2.670	1.820
3-methylbutan-1-ol	7.122	13.027	-1.898	-1.758	-2.920	-4.420
3-methylbutan-2-one	9.913	12.779	-4.400	-2.186	-2.930	-3.240
3-methylbutanoic-acid	1.968	-	-9.420	-	-5.510	-6.090
3-methylheptane	25.647	27.708	1.351	5.674	3.290	2.970
3-methylhexane	22.973	25.009	1.332	5.205	2.760	2.710
3-methylpentane	20.253	22.182	1.246	4.665	2.720	2.510
3-methylpyridine	8.864	11.280	-4.182	-2.466	-3.190	-4.770
3-nitroaniline	1.677	8.599	-8.993	-5.865	-8.240	-8.840
3-nitrophenol	-0.787	-	-9.320	-	-7.660	-9.620
3-nitrotoluene	12.030	15.213	-4.431	-1.480	-3.160	-3.450
3-phenylpropanol	9.252	14.925	-5.732	-3.961	-5.500	-6.920
4-acetylpyridine	4.594	8.516	-9.192	-6.934	-7.630	-7.620
4-bromophenol	2.800	10.426	-7.346	-4.396	-5.470	-7.130
4-bromotoluene	16.127	18.580	-2.019	0.927	0.040	-1.390
4-chloro-3-methylphenol	4.849	11.785	-7.176	-4.029	-4.900	-6.790
4-chloroaniline	4.302	10.338	-7.218	-4.017	-5.280	-5.900
4-chlorophenol	0.897	-	-7.659	-	-5.360	-7.030
4-cyanophenol	-2.853	6.595	-11.203	-7.418	-7.610	-10.170
4-cyanopyridine	4.793	8.881	-7.364	-4.519	-4.970	-6.020
4-ethylphenol	4.932	-	-5.560	-	-5.080	-6.130
4-ethylpyridine	11.549	14.278	-4.142	-1.873	-2.870	-4.730

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Compound	$\Delta\Theta^{\mu VT}_{MDFT}$	$\Delta\Theta^{\mu VT}_{3DRISM}$	ΔG^{NPT}_{MDFT}	ΔG^{NPT}_{3DRISM}	ΔG_{MD}	ΔG_{expt}
4-ethyltoluene	18.322	20.670	-1.761	1.214	-0.050	-0.950
4-fluorophenol	0.663	8.082	-7.990	-4.779	-4.990	-6.190
4-formylpyridine	1.771	5.942	-9.249	-7.125	-7.310	-7.000
4-isopropyltoluene	21.324	23.830	-1.478	2.162	0.200	-0.680
4-methoxyacetophenone	8.359	12.541	-9.140	-6.553	-6.290	-4.400
4-methoxyaniline	2.791	8.637	-9.288	-6.631	-6.920	-7.480
4-methyl-1h-imidazole	-1.979	2.973	-9.774	-7.917	-7.990	-10.270
4-methylacetophenone	11.525	14.678	-6.570	-4.206	-4.820	-4.700
4-methylbenzaldehyde	8.617	12.368	-6.532	-4.196	-4.900	-4.270
4-methylpentan-2-ol	13.296	16.912	-2.820	-0.009	-2.750	-3.730
4-methylpentan-2-one	12.909	15.665	-4.195	-1.610	-2.960	-3.050
4-methylpyridine	8.543	11.015	-4.362	-2.670	-3.410	-4.930
4-nitroaniline	-1.368	7.118	-10.645	-7.250	-9.230	-10.270
4-nitrophenol	-2.021	-	-6.808	-	-8.220	-10.640
4-tert-butylphenol	9.292	17.732	-5.701	-3.142	-5.540	-5.910
E-12-dichloroethene	10.006	11.955	-0.680	1.447	1.200	-0.780
E-but-2-enal	4.497	7.836	-5.478	-3.831	-3.660	-4.220
E-hept-2-ene	21.467	23.591	0.977	4.444	2.830	1.680
E-hex-2-enal	10.690	14.223	-4.862	-2.112	-3.220	-3.680
E-oct-2-enal	16.401	-	-4.602	-	-2.470	-3.430
NN-dimethyl-p-methoxybenzamide	8.792	13.115	-12.049	-9.314	-9.290	-11.010
NN-dimethyl-p-methylbenzamide	11.575	14.925	-9.600	-7.163	-7.510	-9.760
NN-dimethylaniline	10.826	13.640	-5.522	-3.842	-4.700	-3.450
NN-dimethylbenzamide	8.852	12.263	-9.636	-7.572	-7.980	-9.290
NN-dimethylformamide	0.772	3.952	-7.868	-6.821	-6.860	-7.810
N-acetylpyrrolidine	6.434	9.434	-8.317	-6.559	-7.970	-9.800
N-methyl-N–222-trifluoroethyl–aniline	12.375	-	-7.974	-	-3.690	-1.920
N-methylacetamide	-3.037	2.254	-9.276	-8.507	-8.390	-10.000
N-methylaniline	5.229	10.367	-4.526	-4.606	-5.740	-4.690
N-methylmorpholine	7.646	9.492	-5.062	-4.412	-5.870	-6.320
N-methylpiperazine	5.237	7.548	-5.025	-6.308	-8.300	-7.770
N-methylpiperidine	13.395	14.693	-2.684	-1.149	-3.210	-3.880
Z-12-dichloroethene	8.197	10.599	-1.953	0.222	0.310	-1.170
Z-pent-2-ene	15.705	17.482	0.772	3.216	2.550	1.310
acenaphthene	14.670	17.847	-5.454	-2.343	-3.510	-3.150
acetaldehyde	0.867	3.771	-5.074	-3.998	-3.390	-3.500
acetonitrile	1.589	4.329	-4.634	-3.159	-1.670	-3.880
acetophenone	8.606	11.841	-6.727	-4.718	-5.070	-4.580
alpha-methylstyrene	15.545	18.156	-2.787	-0.117	-1.260	-1.240
ammonia	-4.613	-1.434	-4.856	-4.848	-4.040	-4.290
aniline	2.372	7.728	-7.222	-4.906	-5.920	-5.490
anisole	9.683	12.670	-4.595	-2.354	-2.300	-2.450
anthracene	14.668	18.443	-7.272	-3.978	-5.390	-3.950
azetidine	4.506	6.298	-3.550	-3.283	-3.410	-5.560
benzaldehyde	5.726	9.351	-6.686	-4.785	-4.990	-4.020
benzamide	-2.670	3.955	-12.625	-10.497	-10.190	-11.000
benzene	9.505	11.684	-2.170	-0.691	-0.700	-0.860
benzonitrile	8.930	12.394	-4.632	-2.113	-2.740	-4.210

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Compound	$\Delta\Theta^{\mu VT}_{MDFT}$	$\Delta\Theta^{\mu VT}_{3DRISM}$	ΔG^{NPT}_{MDFT}	ΔG^{NPT}_{3DRISM}	ΔG_{MD}	ΔG_{expt}
benzotrifluoride	13.591	17.078	-2.907	0.259	-0.550	-0.250
benzyl-alcohol	6.476	10.918	-5.914	-3.481	-5.410	-6.620
benzyl-bromide	14.232	16.887	-3.187	-0.360	-1.140	-2.380
benzyl-chloride	12.219	15.329	-3.612	-0.844	-1.560	-1.930
biphenyl	17.739	19.929	-3.653	-1.133	-3.390	-2.660
bis-2-chloroethyl–ether	8.694	-	-6.284	-	-1.860	-4.230
bromobenzene	13.218	15.532	-2.195	0.264	-0.370	-1.460
bromoethane	10.568	12.299	-0.545	1.440	0.930	-0.740
bromomethane	7.876	9.421	-0.545	0.931	1.090	-0.820
bromotrifluoromethane	12.188	13.561	0.727	2.561	2.030	1.790
but-1-ene	13.416	15.137	0.906	2.979	2.480	1.380
but-1-yne	9.819	11.485	-0.826	1.011	1.930	-0.160
buta-13-diene	11.036	13.057	0.110	1.906	1.930	0.610
butan-1-ol	4.000	10.781	-1.857	-1.902	-3.140	-4.720
butan-2-ol	7.375	10.858	-3.740	-1.873	-3.120	-4.620
butanenitrile	7.825	10.676	-3.904	-1.589	-1.410	-3.640
butanone	6.700	9.696	-4.688	-2.728	-2.970	-3.710
butyraldehyde	6.700	9.696	-4.688	-2.728	-3.010	-3.180
chlorobenzene	11.783	14.230	-2.218	0.147	-0.600	-1.120
chlorodifluoromethane	4.631	8.047	-2.846	-0.460	-0.040	-0.500
chloroethane	8.624	10.575	-0.916	0.920	0.780	-0.630
chloroethylene	8.083	9.939	-0.573	1.039	1.220	-0.590
chlorofluoromethane	4.178	7.038	-2.613	-0.732	-0.220	-0.770
chloromethane	5.889	7.755	-0.907	0.483	0.810	-0.550
cis-12-dimethylcyclohexane	22.621	24.361	0.837	4.719	2.050	1.580
cyanobenzene	8.930	12.394	-4.632	-2.113	-2.380	-4.100
cyclohepta-135-triene	12.117	14.252	-2.101	-0.289	0.150	-0.990
cycloheptanol	9.744	15.793	-3.229	-1.211	-4.150	-5.480
cyclohexane	17.272	18.888	0.678	3.648	1.670	1.230
cyclohexanol	7.419	12.986	-3.500	-2.155	-4.260	-5.460
cyclohexanone	9.907	12.439	-4.754	-2.454	-3.840	-4.910
cyclohexene	15.276	16.961	0.138	2.545	1.560	0.370
cyclohexylamine	12.473	14.022	-2.817	-1.475	-3.940	-4.590
cyclopentane	14.732	16.293	0.663	3.195	1.530	1.200
cyclopentanol	4.454	10.107	-2.143	-2.795	-4.150	-5.490
cyclopentanone	7.404	9.868	-4.677	-2.795	-3.710	-4.700
cyclopentene	12.681	14.222	0.095	2.070	1.380	0.560
cyclopropane	10.791	12.228	1.101	2.743	2.640	0.750
decan-1-ol	21.969	-	-4.649	-	-2.490	-3.640
decan-2-one	23.790	-	-4.128	-	-1.980	-2.340
di-isopropyl-sulfide	18.225	20.892	-1.793	1.629	0.100	-1.210
di-n-butyl-ether	22.918	25.270	-1.203	2.536	0.590	-0.830
di-n-butylamine	20.926	-	-2.375	-	-1.630	-3.240
di-n-propyl-ether	17.290	19.588	-1.368	1.362	0.210	-1.160
di-n-propyl-sulfide	19.302	21.836	-1.371	2.068	0.490	-1.280
di-n-propylamine	15.377	17.630	-2.491	-0.596	-2.260	-3.650
dibromomethane	10.677	12.268	-1.027	1.055	0.870	-1.960
dichloromethane	6.532	8.808	-1.894	0.029	0.230	-1.310

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Compound	$\Delta\Theta^{\mu VT}_{MDFT}$	$\Delta\Theta^{\mu VT}_{3DRISM}$	ΔG^{NPT}_{MDFT}	ΔG^{NPT}_{3DRISM}	ΔG_{MD}	ΔG_{expt}
diethoxymethoxybenzene	20.458	-	-6.120	-	-4.440	-5.230
diethyl-disulfide	15.762	18.482	-2.099	1.119	-0.070	-1.640
diethyl-ether	11.116	13.347	-1.896	-0.022	-0.700	-1.590
diethyl-malonate	8.685	-	-10.062	-	-6.450	-6.000
diethyl-succinate	14.028	-	-8.170	-	-8.470	-5.710
diethyl-sulfide	13.461	15.982	-1.631	1.026	0.210	-1.460
diethylamine	9.096	11.644	-2.443	-1.838	-2.720	-4.070
diiodomethane	9.315	11.777	-3.419	-0.640	-0.740	-2.490
diisopropyl-ether	17.606	19.790	-1.278	1.390	-0.110	-0.530
diisopropylamine	14.888	-	-2.325	-	-1.970	-3.220
dimethoxymethane	7.621	9.610	-2.981	-1.641	-2.690	-2.930
dimethyl-disulfide	12.858	14.643	-0.236	2.082	1.480	-1.830
dimethyl-ether	5.418	7.302	-2.156	-1.108	-0.850	-1.910
dimethyl-sulfate	2.289	-	-8.847	-	-7.850	-5.100
dimethyl-sulfide	8.242	10.331	-1.436	0.340	0.260	-1.610
dimethyl-sulfone	-4.656	-0.921	-11.838	-11.146	-10.360	-10.080
dimethyl-sulfoxide	-2.318	1.193	-9.847	-8.960	-8.320	-8.710
dimethylamine	3.337	5.427	-3.344	-3.021	-3.110	-4.290
ethanamide	-6.810	-1.460	-10.574	-9.682	-8.620	-9.710
ethane	9.530	10.840	1.113	2.557	2.580	1.830
ethanethiol	6.549	9.337	-2.292	-0.412	-0.400	-1.140
ethanol	-0.400	4.457	-5.526	-3.534	-3.450	-5.000
ethene	7.906	9.273	0.832	1.926	2.360	1.280
ethyl-acetate	8.032	10.660	-4.431	-2.637	-3.230	-2.940
ethyl-benzoate	13.631	15.839	-5.883	-3.721	-4.680	-3.640
ethyl-butanoate	13.632	16.231	-4.169	-1.741	-3.040	-2.490
ethyl-formate	5.152	7.922	-4.350	-2.810	-2.990	-2.560
ethyl-hexanoate	19.315	-	-4.041	-	-2.800	-2.230
ethyl-pentanoate	16.414	18.964	-4.140	-1.295	-3.090	-2.490
ethyl-phenyl-ether	13.120	15.882	-4.143	-1.649	-2.010	-2.220
ethyl-propanoate	10.661	13.255	-4.423	-2.417	-3.390	-2.680
ethylamine	2.958	5.675	-3.377	-2.805	-3.140	-4.500
ethylbenzene	15.408	17.781	-1.873	0.751	-0.590	-0.790
fluorene	15.506	18.640	-5.887	-2.875	-4.290	-3.350
fluorobenzene	10.846	13.528	-2.011	0.341	-0.070	-0.800
fluoromethane	4.365	6.442	-1.056	0.156	0.790	-0.220
formaldehyde	-2.101	0.953	-5.230	-4.320	-3.220	-2.750
halothane	13.465	16.054	-1.509	1.650	0.700	-0.110
hept-1-ene	21.649	23.740	1.067	4.586	2.970	1.660
hept-1-yne	18.286	20.197	-0.536	2.709	2.280	0.600
heptan-1-ol	14.949	20.039	-4.080	0.478	-2.720	-4.210
heptan-2-one	15.485	18.516	-4.283	-1.192	-2.800	-3.040
heptan-4-one	15.867	18.728	-3.933	-0.896	-2.680	-2.920
heptanal	14.892	18.459	-4.519	-1.067	-2.630	-2.670
hex-1-ene	18.776	20.775	0.974	3.992	2.590	1.580
hex-1-yne	18.285	20.176	0.686	3.814	2.100	0.290
hexa-15-diene	17.329	19.163	0.727	3.099	2.440	1.010
hexafluoropropene	14.513	17.111	0.202	3.047	2.290	-3.760

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Compound	$\Delta\Theta^{\mu VT}_{MDFT}$	$\Delta\Theta^{\mu VT}_{3DRISM}$	ΔG^{NPT}_{MDFT}	ΔG^{NPT}_{3DRISM}	ΔG_{MD}	ΔG_{expt}
hexan-1-ol	12.139	17.161	-4.025	-0.334	-3.030	-4.400
hexan-2-one	12.745	15.835	-4.318	-1.636	-2.770	-3.280
hexan-3-ol	12.285	16.797	-2.926	-0.609	-2.630	-4.060
hexanal	12.265	15.560	-4.562	-1.639	-2.960	-2.810
hexanoic-acid	4.219	-	-3.840	-	-5.080	-6.210
hydrazine	-11.267	-6.528	-10.173	-10.784	-7.100	-9.300
hydrogen-sulfide	-1.501	2.300	-3.735	-2.197	-1.170	-0.700
imidazole	-4.684	0.138	-9.546	-8.234	-7.850	-9.630
indane	15.174	17.435	-2.500	0.032	-1.700	-1.460
iodobenzene	14.140	16.407	-2.272	0.386	-0.340	-1.740
iodoethane	9.817	11.782	-1.862	0.212	-0.100	-0.740
iodomethane	6.831	8.842	-2.062	-0.340	0.030	-0.890
isoamyl-acetate	15.930	18.552	-4.403	-1.483	-3.050	-2.210
isoamyl-formate	12.522	15.847	-4.674	-1.769	-3.390	-2.130
isobutyl-acetate	13.826	16.429	-4.105	-1.524	-2.800	-2.360
isobutyl-formate	10.245	13.574	-4.485	-1.932	-3.210	-2.220
isobutyl-isobutanoate	19.863	-	-3.524	-	-2.550	-1.690
isobutylbenzene	20.830	23.198	-1.476	1.981	0.000	0.160
isobutyraldehyde	7.176	9.788	-4.337	-2.580	-2.930	-2.860
isoflurane	8.175	14.502	-6.187	-1.353	-1.380	0.100
isopropyl-acetate	10.521	13.346	-4.585	-2.367	-2.920	-2.640
isopropyl-formate	7.693	10.547	-4.397	-2.469	-2.640	-2.020
isopropylbenzene	17.991	20.389	-1.835	1.217	-0.310	-0.300
m-bis-trifluoromethyl–benzene	15.504	19.969	-4.596	-0.249	-1.580	1.070
m-cresol	3.297	10.177	-8.108	-4.255	-5.280	-5.490
m-xylene	15.353	17.804	-1.948	0.575	-0.170	-0.830
methane	6.890	8.039	1.148	2.085	2.540	1.990
methanesulfonyl-chloride	-0.849	2.863	-8.772	-7.050	-6.330	-4.870
methanethiol	3.923	6.592	-2.232	-0.718	-0.260	-1.240
methanol	-4.840	1.726	-2.391	-3.841	-3.480	-5.100
methoxyflurane	13.298	16.152	-2.521	0.704	-0.710	-1.120
methyl-acetate	4.372	6.788	-5.109	-3.909	-3.730	-3.130
methyl-benzoate	10.168	12.726	-6.298	-4.319	-5.060	-3.920
methyl-butanoate	10.536	12.986	-4.447	-2.434	-3.320	-2.830
methyl-chloroacetate	4.974	8.183	-5.863	-3.920	-3.920	-4.000
methyl-cyanoacetate	0.821	5.552	-9.128	-6.701	-5.510	-6.720
methyl-cyclohexanecarboxylate	16.047	18.036	-4.526	-1.756	-4.290	-3.300
methyl-cyclohexyl-ketone	15.099	17.924	-4.709	-1.604	-3.900	-3.900
methyl-cyclopropanecarboxylate	8.828	11.629	-4.708	-2.729	-4.490	-4.100
methyl-cyclopropyl-ketone	8.930	11.494	-4.061	-2.214	-3.740	-4.610
methyl-ethyl-ether	8.299	10.451	-2.030	-0.506	-0.820	-2.100
methyl-ethyl-sulfide	10.866	13.200	-1.526	0.681	0.340	-1.500
methyl-formate	1.984	4.790	-4.652	-3.440	-3.170	-2.780
methyl-hexanoate	16.160	18.771	-4.302	-1.404	-3.020	-2.490
methyl-isopropyl-ether	11.007	13.005	-1.984	-0.145	-0.750	-2.010
methyl-methanesulfonate	0.448	3.268	-8.919	-7.953	-8.290	-4.870
methyl-octanoate	21.723	24.875	-4.172	-0.171	-2.940	-2.040
methyl-p-methoxybenzoate	10.725	13.850	-8.449	-5.783	-6.320	-5.330

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Compound	$\Delta\Theta^{\mu VT}_{MDFT}$	$\Delta\Theta^{\mu VT}_{3DRISM}$	ΔG^{NPT}_{MDFT}	ΔG^{NPT}_{3DRISM}	ΔG_{MD}	ΔG_{expt}
methyl-p-nitrobenzoate	-8.505	-0.397	-19.598	-18.989	-6.390	-6.880
methyl-pentanoate	13.300	16.034	-4.441	-1.903	-3.510	-2.560
methyl-propanoate	7.479	9.897	-4.762	-3.227	-3.830	-2.930
methyl-propyl-ether	11.330	13.442	-1.825	0.065	-0.410	-1.660
methyl-t-butyl-ether	13.608	15.569	-1.879	0.281	-0.600	-2.210
methyl-tert-butyl-ether	13.607	15.568	-1.880	0.280	-0.680	-2.210
methyl-trifluoroacetate	8.838	12.066	-3.319	-0.943	-1.390	-1.100
methyl-trimethylacetate	13.735	16.267	-4.007	-1.449	-2.990	-2.400
methylamine	-0.521	2.205	-3.985	-3.804	-3.440	-4.550
methylcyclohexane	19.991	21.754	0.768	4.162	1.820	1.700
methylcyclopentane	17.573	19.205	0.777	3.757	2.120	1.590
morpholine	3.623	6.179	-5.825	-5.202	-6.280	-7.170
n-butane	14.956	16.583	1.182	3.629	2.540	2.070
n-butanethiol	11.981	15.161	-2.124	0.693	-0.120	-0.990
n-butyl-acetate	13.301	16.138	-4.475	-1.807	-3.170	-2.640
n-butylacetamide	5.171	10.594	-10.252	-7.105	-8.140	-9.310
n-butylamine	7.821	10.961	-3.539	-2.173	-2.820	-4.240
n-butylbenzene	21.131	-	-1.622	-	-0.300	-0.400
n-decane	31.725	-	1.587	-	3.430	3.160
n-heptane	23.327	25.291	1.393	5.244	3.200	2.670
n-heptylamine	16.980	20.538	-3.056	0.238	-2.720	-3.790
n-hexane	20.411	22.573	1.276	4.779	3.050	2.480
n-hexyl-acetate	18.810	-	-4.355	-	-2.970	-2.260
n-hexylamine	13.915	17.491	-3.110	-0.433	-2.540	-3.950
n-hexylbenzene	26.593	-	-1.536	-	0.240	-0.040
n-nonane	28.825	-	1.486	-	3.320	3.130
n-octane	26.129	28.308	1.448	5.796	3.130	2.880
n-octylamine	18.892	-	-3.300	-	-2.380	-3.650
n-pentane	17.683	19.543	1.245	4.172	2.670	2.320
n-pentyl-acetate	16.067	18.951	-4.385	-1.346	-2.830	-2.510
n-pentyl-propanoate	19.277	-	-4.013	-	-3.360	-2.110
n-pentylamine	10.561	13.891	-3.727	-1.626	-2.990	-4.090
n-pentylbenzene	23.803	-	-1.597	-	0.050	-0.230
n-pentylcyclopentane	28.558	-	1.044	-	2.390	2.550
n-propanethiol	9.504	12.426	-2.122	0.295	-0.310	-1.060
n-propyl-acetate	10.784	13.531	-4.386	-2.169	-3.330	-2.790
n-propyl-butyrate	16.628	19.222	-3.941	-1.089	-2.880	-2.280
n-propyl-formate	7.238	10.420	-4.729	-2.732	-3.500	-2.480
n-propyl-propanoate	13.761	15.891	-4.158	-1.973	-2.950	-2.440
n-propylamine	5.763	8.538	-3.449	-2.279	-3.050	-4.390
n-propylbenzene	18.142	20.477	-1.760	1.220	0.010	-0.530
n-propylcyclopentane	22.953	24.829	0.895	4.842	2.150	2.130
naphthalene	11.711	15.093	-4.998	-2.353	-3.340	-2.400
nitrobenzene	8.863	11.941	-4.795	-2.251	-3.400	-4.120
nitroethane	6.378	8.862	-3.283	-1.163	-1.730	-3.710
nitromethane	3.042	5.523	-3.691	-1.931	-2.030	-4.020
non-1-ene	27.226	-	1.186	-	2.910	2.060
nonan-1-ol	17.731	-	-1.249	-	-2.540	-3.880

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Compound	$\Delta\Theta^{\mu VT}_{MDFT}$	$\Delta\Theta^{\mu VT}_{3DRISM}$	ΔG^{NPT}_{MDFT}	ΔG^{NPT}_{3DRISM}	ΔG_{MD}	ΔG_{expt}
nonan-2-one	20.996	-	-4.206	-	-2.510	-2.490
nonan-5-one	21.391	-	-3.858	-	-2.340	-2.640
nonanal	20.502	-	-4.427	-	-2.510	-2.070
o-cresol	2.833	10.039	-7.314	-4.355	-5.090	-5.870
o-toluidine	5.886	10.803	-6.574	-4.138	-5.370	-5.530
o-xylene	15.001	17.476	-2.085	0.474	-0.520	-0.900
oct-1-ene	24.429	26.621	1.140	5.095	2.770	1.920
oct-1-yne	21.064	23.117	-0.477	3.275	2.460	0.710
octan-1-ol	14.847	-	-0.958	-	-2.650	-4.090
octan-2-one	18.212	-	-4.251	-	-2.300	-2.880
octanal	17.624	21.332	-4.554	-0.611	-2.570	-2.290
p-cresol	2.407	-	-8.281	-	-5.360	-6.130
p-dibromobenzene	17.225	19.588	-2.075	1.451	-0.010	-2.300
p-toluidine	5.292	10.784	-7.086	-4.250	-5.560	-5.570
p-xylene	15.296	17.718	-1.960	0.560	-0.670	-0.800
pent-1-ene	16.027	17.936	0.901	3.460	2.440	1.680
pent-1-yne	12.691	14.458	-0.689	1.621	1.930	0.010
penta-14-diene	14.040	16.055	0.393	2.522	2.180	0.930
pentachloroethane	16.580	18.721	-1.284	2.224	0.310	-1.390
pentan-1-ol	8.661	13.868	-2.198	-1.008	-3.140	-4.570
pentan-2-ol	8.970	13.730	-4.417	-1.458	-2.870	-4.390
pentan-2-one	9.820	12.809	-4.432	-2.175	-3.290	-3.520
pentan-3-ol	8.493	14.094	-1.450	-0.869	-2.950	-4.350
pentan-3-one	9.959	12.707	-4.301	-2.228	-2.940	-3.410
pentanal	9.297	12.655	-4.720	-2.161	-2.960	-3.030
pentanenitrile	10.571	13.720	-3.835	-0.928	-1.240	-3.520
pentanoic-acid	1.955	-	-9.619	-	-5.370	-6.160
phenanthrene	15.035	-	-7.147	-	-5.150	-3.880
phenol	-1.110	-	-7.906	-	-5.670	-6.610
phenyl-formate	5.525	9.996	-7.889	-5.016	-4.830	-3.820
phenyl-methyl-sulfide	13.607	16.379	-3.147	-0.409	-1.210	-2.730
phenyl-trifluoroethyl-ether	9.919	15.970	-7.684	-3.274	-2.930	-1.290
piperazine	1.776	4.140	-6.830	-7.182	-8.340	-7.400
piperidine	9.293	11.071	-3.326	-2.227	-3.460	-5.110
prop-2-en-1-ol	1.999	7.156	-1.536	-2.367	-3.230	-5.030
propan-1-ol	2.610	7.950	-2.433	-2.461	-3.120	-4.850
propan-2-ol	3.215	8.148	-3.313	-2.290	-3.280	-4.740
propane	12.177	13.772	1.123	3.104	2.560	1.960
propanenitrile	4.920	7.626	-4.127	-2.259	-1.270	-3.840
propanoic-acid	-5.568	3.524	-4.191	-6.307	-6.410	-6.460
propanone	4.034	6.877	-4.848	-3.410	-3.360	-3.800
propene	10.417	12.077	0.739	2.337	2.440	1.320
propionaldehyde	3.745	6.750	-4.855	-3.343	-3.080	-3.430
propyne	6.940	8.416	-1.000	0.355	1.790	-0.480
pyrene	14.858	17.928	-8.959	-5.735	-6.620	-4.520
pyridine	5.579	7.769	-4.579	-3.442	-3.450	-4.690
pyrrole	0.886	5.042	-5.805	-4.429	-3.870	-4.780
pyrrolidine	6.077	8.055	-3.619	-3.060	-3.910	-5.480

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Compound	$\Delta\Theta^{\mu VT}_{MDFT}$	$\Delta\Theta^{\mu VT}_{3DRISM}$	ΔG^{NPT}_{MDFT}	ΔG^{NPT}_{3DRISM}	ΔG_{MD}	ΔG_{expt}
quinoline	9.605	12.373	-6.200	-4.040	-4.870	-5.720
sec-butylbenzene	20.691	23.153	-1.577	1.813	0.040	-0.450
styrene	13.101	15.725	-2.679	-0.445	-1.320	-1.240
teflurane	11.337	14.340	-2.120	1.037	0.460	0.500
tert-butylbenzene	20.420	22.571	-1.783	1.399	-0.420	-0.440
tetrachloroethene	16.080	17.173	0.444	2.986	1.410	0.100
tetrachloromethane	14.231	15.293	0.365	2.607	1.410	0.080
tetrafluoromethane	9.768	11.361	1.001	2.503	2.420	3.120
tetrahydrofuran	7.896	9.834	-2.843	-1.316	-2.070	-3.470
tetrahydropyran	11.145	13.011	-2.354	-0.343	-1.780	-3.120
thiophene	8.789	10.787	-1.758	-0.169	-0.340	-1.420
thiophenol	9.045	12.875	-4.021	-1.312	-1.430	-2.550
toluene	12.393	14.749	-2.070	-0.046	-0.710	-0.890
trans-14-dimethylcyclohexane	22.802	24.470	0.865	4.733	2.050	2.110
triacetyl-glycerol	7.461	-	-12.892	-	-13.310	-8.840
tribromomethane	15.094	16.224	-0.427	2.111	0.880	-2.130
trichloroethene	12.125	14.011	-0.741	1.721	0.990	-0.440
trichloromethane	9.163	11.410	-1.584	0.846	0.320	-1.080
triethyl-phosphate	11.126	-	-10.713	-	-10.060	-7.540
triethylamine	15.032	16.664	-1.824	-1.007	-1.830	-3.220
trimethoxy-methane	7.679	10.583	-5.407	-3.781	-4.060	-4.420
trimethoxymethylbenzene	17.443	19.851	-5.835	-3.560	-5.830	-4.040
trimethyl-phosphate	1.320	-	-11.700	-	-10.590	-8.700
trimethylamine	7.380	9.063	-2.621	-1.979	-2.320	-3.200
undecan-2-one	26.558	-	-4.062	-	-2.120	-2.150